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Purdue University  
Department of Physics

SEMICONDUCTOR RESEARCH  
FIFTH QUARTERLY REPORT

October 1, 1961 to December 31, 1961

Contract DA 36-039-sc-87394

PURDUE RESEARCH FOUNDATION  
and  
UNITED STATES SIGNAL CORPS  
PRF 2641

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## I. ELECTRICAL AND OPTICAL PROPERTIES

### INFRARED MEASUREMENT OF HOT CARRIER TEMPERATURE IN p-TYPE GE

W. Pinson and R. Bray

Since the last report a review and analysis of the methods and results of the infrared-hot carrier experiment have been completed, which indicated the desirability of making many modifications in the apparatus and improvements in the procedure for taking the data and analysing it. Much of the new equipment has now been designed, built and tested. The highlights of the above work will be outlined below.

The change in absorption coefficient,  $\Delta \alpha$ , with pulsed electric field strength will be directly determined by measuring the ratio of the pulse change in transmission,  $\Delta I_T$ , due to a pulsed field, to the transmission,  $I_T$ , at zero field. The expression relating  $\Delta \alpha$  to this ratio is a relatively simple one and contains all the necessary corrections for multiple reflections and the fact the light path through the sample is greater than the region subjected to high fields. The latter geometrical consideration is due to the presence of large area end contacts to eliminate injection effects at high fields. The new procedures also eliminate possible errors due to long time variations in light intensity and detector sensitivity.

However, the ratio  $\Delta I_T/I_T$  cannot be measured directly because of 1) the non-linearity of the detector, 2) the long excited carrier lifetime  $\tau$  of the InSb detector ( $\tau >$  pulse length), 3) lattice heating effects produced by the pulse in the Ge sample. Improved techniques and analyses for all these effects have been developed.

Our determination of the absorption coefficient  $\alpha$  as a function of wavelength, particularly at 77°K, and the changes in  $\alpha$  with lattice temperature had not been too successful for Ge with around  $3 \times 10^{15}$  holes/cc in the 2 to 5 micron region. The main source of the difficulty in measurement lies in the small values of  $\alpha$  in this range ( $0.01 \text{ cm}^{-1}$  to  $1.0 \text{ cm}^{-1}$ ), necessitating the use of long samples with the attendant problems of uniform cooling and optical defocussing. We have, therefore, built an exchange gas cell to cool the samples, and switched to a technique of making comparative transmission measurements of our p-type sample with a pure n-type Ge sample of exactly the same length, resulting in an improvement of our measurements of  $\alpha$ . As the several published<sup>1,2</sup> values of the magnitude of  $\alpha$  disagree by 30% or more, it is necessary for us to remeasure absorption cross sections more carefully.

1. H. B. Briggs and R. C. Fletcher, Phys. Rev. 91, 1342 (1953).
2. R. Newman and W. W. Tyler, Phys. Rev. 105, 885 (1957).

### GALVANOMAGNETIC PROPERTIES OF n-GaP

W. M. Becker and H. Y. Fan

Optical measurements by Edwards and Drickamer<sup>1</sup> indicate that the lowest conduction band in n-GaP is silicon-like, with the band minima lying along [100] directions. However, no extensive electrical measurements are available relating to this result. We have begun an investigation into the galvanomagnetic properties of this material using sulphur-doped single crystals supplied by Bell Telephone Laboratories.

Initial work showed that the usual solder or pressure contacts resulted in unsatisfactory non-ohmic high resistance contacts. Successful contact to the samples was finally made as follows: The appropriate regions of the sample surface were painted with Hanovia #38 silver paste to which a small amount of tellurium had been added. The sample was then heated in a hydrogen atmosphere at  $\sim 600^{\circ}\text{C}$  for one hour, after which the silver paste was removed. Low resistance, ohmic contacts were obtained by soldering indium directly to the diffused areas.

Hall effect, conductivity, and magnetoresistance were measured on a sample having a room temperature Hall coefficient  $R = -19 \text{ cm}^3/\text{coul.}$  and  $\mu_H = 131 \text{ cm}^2/\text{volt-sec.}$  At  $77^{\circ}\text{K}$ , the Hall coefficient rises to  $R = -2.2 \times 10^4 \text{ cm}^3/\text{coul.}$  and  $\mu_H = 333 \text{ cm}^2/\text{volt-sec.}$  Transverse magnetoresistance was observed neither at room temperature for fields up to 22,000 gauss, nor at  $77^{\circ}\text{K}$  for fields up to 13,500 gauss. Based on the errors in the measurements, the room temperature value was estimated to be of the order of  $\Delta\rho/\rho \sim 0.1\%$  at the highest field; the estimated value at  $77^{\circ}\text{K}$  was  $\Delta\rho/\rho \sim 0.1\%$ . Measurements at higher fields should yield more reliable data for the determination of the magnetoresistance coefficients.

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1. A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids 11, 140 (1959).



## INFRARED ABSORPTION IN GaSb

E. J. Johnson and H. Y. Fan

Three exciton like lines observed on the fundamental absorption edge of GaSb at  $4.5^{\circ}\text{K}$  have been described in previous progress reports<sup>1,2</sup>. These lines have now been observed at  $1.7^{\circ}\text{K}$  where they become sharper and more intense. The lines at  $1.7^{\circ}\text{K}$  are shown in Fig. 1. The  $\alpha$  line is probably associated with the formation of a free exciton. A different interpretation is necessary for the  $\beta$  and  $\gamma$  lines. The possibility under consideration is that the latter lines might be due to the formation of excitons near imperfections<sup>2</sup>. The obvious test for this interpretation would be to look for variation in the strengths of the lines in different samples. In an attempt to verify this hypothesis, measurement was made on a sample having a somewhat smaller Hall coefficient. The result showed that the  $\gamma$  peak broadened into a step without appreciably increasing the strength. It is possible that the excess impurity in the sample is not of the type that gives rise to the  $\gamma$  peak. Preliminary measurements of the Zeeman effect have been made on the  $\beta$  and  $\gamma$  lines. The results obtained are shown in Fig. 2 and can be summarized as follows:

1. Each line splits into two components.
2. Each component occurs at higher photon energy than the line at zero magnetic field.
3. The spectra with polarization  $E \parallel H$  is identical to the spectra with  $E \perp H$ .
4. The observed splitting is too large to be accounted for by spin.

These results need further study, but they seem to indicate effects of degenerate valence bands at  $k = 0$ .

- 
1. E. J. Johnson and H. Y. Fan, Semiconductor Research, Third Quarterly Report, April 1, 1961 to June 30, 1961.
  2. E. J. Johnson and H. Y. Fan, Semiconductor Research, Final Report, October 1, 1960 to September 30, 1961.

## RECOMBINATION RADIATION IN GALLIUM ANTIMONIDE

I. Filinski and H. Y. Fan

Investigation of recombination radiation in GaSb has been continued. In the previous measurements at liquid helium temperature, there was some uncertainty regarding sample temperatures. The measurements were, therefore, repeated both at liquid nitrogen and liquid helium temperatures by actually immersing the sample in the coolant. The present results show that the position of peaks observed at liquid helium temperature for pure p-type samples are  $0.752 \text{ ev} \pm 0.002 \text{ ev}$ ,  $0.779 \pm 0.02 \text{ ev}$ , and  $0.796 \pm 0.02 \text{ ev}$ . The half width of observed peaks is  $\sim 0.006 - 0.008 \text{ ev}$  and is larger than the resolution used viz  $\sim 0.002 \text{ ev}$ . The relative intensity of  $0.779 \text{ ev}$  to  $0.796 \text{ ev}$  peaks changed from sample to sample even for samples taken from different parts of the same ingot.

The following model has been considered to explain the observed emission and absorption spectra. The  $0.779 \text{ ev}$  and  $0.752 \text{ ev}$  peaks are connected with electron recombination with acceptor centers. The  $0.796 \text{ ev}$  peak is interpreted as exciton recombination at some impurity. This should be compared with the free exciton recombination expected to occur in purest samples with energy  $\sim 0.811 \text{ ev}$  on the basis of absorption measurements of E. J. Johnson and H. Y. Fan reported in this progress report.

## MAGNETORESISTANCE IN N-TYPE GERMANIUM IN THE IMPURITY CONDUCTION RANGE

G. Sadasiv

The transverse magnetoresistance of several n-type Germanium samples has been measured in the temperature range between  $4.2^{\circ}\text{K}$  and  $1.2^{\circ}\text{K}$ , with magnetic fields up to 12,000 oersted. The orientation of the samples and the characteristics at room temperature and at  $77.4^{\circ}\text{K}$  are given in Table I.

TABLE I

Sample	Impurity	< i >	< H >	297° K		77.4° K	
				cm. <sup>3</sup> R coul. <sup>-1</sup>	ρ ohm-cm.	cm. <sup>3</sup> R coul. <sup>-1</sup>	ρ ohm-cm.
1	Sb	001	110	10.5	.00848	13.2	.0109
2	"	001	110	44.3	.0254	70.8	.0247
3	"	011	100	57.4	.0296	92.1	.0251
4a	"	001	110	76.9	.0382	119.7	.0293
5	"	001	110	90.9	.0410	137.5	.0292
6	"	001	110	106.8	.0480	168.2	.0305
7	"	001	110		.0687		.0367
8	As	011	011	18.9	.0144	29.3	.0204
9	"	011	011	25.8	.0167	41.4	.0219

For samples 5 through 9, measurements were also made with the magnetic field along the < 100 > direction. There was no significant difference in the magnetoresistance.

For samples 3, 4a, 5, and 9 the resistivity  $\rho_H$  in a magnetic field H, at temperatures between 4.2°K and 1.2°K, could be described by the relation

$$\rho_H = \rho_0 \exp (\epsilon + \alpha H^2)/kT \quad (1)$$

For sample 2, the same type of relation held for fields greater than 8000 oersted. Sample 6 showed the  $\epsilon_2$  anomaly in the resistivity<sup>1</sup>, and in the  $\epsilon_2$  region the magnetoresistance was described by (1). The values of  $\rho_0$ ,  $\epsilon$ , and  $\alpha$  are given in Table II.

TABLE II

Sample	ρ <sub>0</sub> ohm-cm.	ε ev	α ev oersted <sup>-2</sup>
2	.143	.030 x 10 <sup>-3</sup>	.35 x 10 <sup>-13</sup>
3	.297	.113	1.27
4a	.532	.284	2.35
5	.748	.691	3.53
6	.698	1.25	4.05
9	.223	.635	1.81

In Fig. 3, the values of  $\Delta\epsilon (= \alpha H^2)$  are plotted against  $H^2$  for these samples.

Sample 1 had a negative magnetoresistance, reported in a previous progress report<sup>2</sup>. For sample 7  $\Delta \rho/\rho$  at a constant field decreased as the temperature was lowered, a behaviour similar to that observed in pure samples by Fritzsche<sup>1</sup>.

- 
1. H. Fritzsche, Phys. Rev. 99, 406 (1955).
  2. G. Sadasiv, Semiconductor Research, Third Quarterly Report, April 1 to June 30, 1961.

### CYCLOTRON RESONANCE-5mm APPARATUS

T. Tohver and G. Newell

Some difficulties in the design and construction of 5 mm sample cavities have been overcome. Initially, to facilitate drilling coupling holes and machining sample illumination slits, the cavity had been split into two parts. However, at 5 mm wavelengths, machining imperfections made this impractical; the split interfered with the wall currents and power was lost through the illumination window, both effects combining to lower the Q excessively. An improved design eliminates the split and the illumination window consists of a series of holes beyond cutoff (Fig. 4). The new design has been tested; it gave a cavity Q of  $\sim 2000$  which is quite satisfactory. The variable coupling scheme shown on the accompanying sketch (Fig. 4) also works quite well - varying smoothly from zero coupling to overcoupling between the waveguide and the cavity. These results on the sample cavity and the latest performance data on 5 mm video detectors have permitted a rough estimate of the sensitivity of the equipment. These calculations are included. Also included is a schematic diagram of the microwave circuit with an indication of the sections that have been completed (Fig. 5).

#### Sensitivity Estimate

Optical excitation of the carriers is to be used. The sensitivity of the apparatus will be defined as the minimum number of detectable carriers. Straightforward circuit theory gives for the detected power under optimum cavity matching conditions

$$P_d = P_o \times 0.193 \frac{\Delta Q}{Q_o}$$

$P_d$  - detected power

$P_o$  - power incident on sample cavity

$\Delta Q$  - change in cavity Q due to excited carriers

$Q_o$  - unloaded cavity Q.

Assuming the power lost to the excited carriers is small compared to the wall losses

$$\frac{\Delta Q}{Q_o} \sim \frac{Q_o}{2\omega} \frac{\int_{\text{Sample}} \sigma E^2 dV}{\int_{\text{Cavity}} \epsilon E^2 dV}$$

$\sigma$  - conductivity due to excited carriers only.

For a needle-shaped sample with a diameter small compared to the wavelength and placed parallel to the maximum E-field of a  $TM_{110}$  cavity

$$\int_{\text{Sample}} \sigma E^2 dV \sim \sigma E_{\text{max}}^2 V_{\text{Sample}}$$

and

$$\int_{\text{Cavity}} \epsilon E^2 dV \sim 1/4 \epsilon_o E_{\text{max}}^2 V_{\text{Cavity}}$$

$$\frac{\Delta Q}{Q_o} = \frac{2Q_o}{\omega \epsilon_o} \times \frac{\sigma V_{\text{Sample}}}{V_{\text{Cavity}}}$$

$$\text{Now } \sigma V_{\text{Sample}} = q (\mu_p \Delta p + u_e \Delta n) V_S$$

For an order of magnitude calculation assume

$$\begin{aligned} u_e = u_p &= 10^4 \frac{\text{cm}^2}{\text{volt-sec}} \\ &= 1 \frac{\text{m}^2}{\text{volt-sec}} \end{aligned}$$

Also call

$$\begin{aligned} V_S \times (\Delta p + \Delta n) &= N \\ &= \text{Total number of carriers excited.} \end{aligned}$$

Take  $Q_o \sim 1000$

$$\begin{aligned}\omega &= 3.3 \times 10^{11} \text{ rad/sec} \\ \epsilon_0 &= 8.9 \times 10^{-12} \text{ farad/m} \\ q &= 1.6 \times 10^{-19} \text{ coul} \\ V_{\text{Cavity}} &\sim 100 (\text{mm})^3 = 10^{-7} \text{ m}^3 \\ P_0 &\sim 1 \text{ milliwatt}\end{aligned}$$

$$\text{Then } P_d \sim 2 \times 10^{-13} \text{ N watts.}$$

At this point, the detector characteristics enter.

A crude equivalent circuit<sup>2</sup> for the square law detector is given below

$$\begin{aligned}\text{Typically}^3 \quad \beta &= 0.13 \text{ amps/watt} \\ R_0 &= 15 \text{ K}\end{aligned}$$

Then the signal voltage is given by:

$$V_S = i_S R_0 = \beta P_d R_0 = 2 \times 10^{-13} \text{ N} \times 0.13 \times 15 \times 10^3.$$

$$\text{Thus } V_S \sim 4 \times 10^{-10} \text{ N volts}$$

Assume the 1/f noise voltage across  $R_0$  at 330 c.p.s. is 100 times the thermal noise in  $R_0$ .<sup>2</sup>

Hence

$$V_{\text{noise}} = 100 \times (K T R_0 \Delta f)^{1/2}$$

For a 30 cps bandwidth ( $\Delta f$ )

$$V_n \sim 4 \times 10^{-6} \text{ volts}$$

For the minimum detectable signal

$$V_{\text{signal}}^{\text{min}} = V_{\text{noise}}$$

$$V_S^{\text{min}} = 4 \times 10^{-6} \text{ v} = 4 \times 10^{-10} \text{ N}^{\text{min}}$$

$$\underline{N^{\text{min}} \sim 10^4 \text{ carriers}}$$

1. G. Feher, B.S.T.J. 36, 449 (1957).
2. E. L. Ginzton, Microwave Measurements (McGraw-Hill 1957), p. 117-119.
3. Sylvania D4074 Millimeter Wave Detector (Private Communication)(B. R. Lincoln, Produce Sales Specialist).

## II. IRRADIATION EFFECTS

### ELECTRON PARAMAGNETIC RESONANCE - SILICON

W. Jung and G. Newell

A sample of neutron irradiated crucible grown silicon (sample #2<sup>1</sup>, USSC No. 4, 100  $\Omega$ -cm; ORNL irradiation at  $T \sim 50^\circ\text{C}$ ,  $\phi = 1.4 \times 10^{18}$  nvt) has been carried through an isochronal anneal in the following steps:  $90^\circ$  to  $170^\circ\text{C}$  in  $10^\circ$  steps for 30 minutes;  $170^\circ$  to  $185^\circ\text{C}$  in  $5^\circ$  steps for 30 minutes; and  $200^\circ$  to  $500^\circ\text{C}$  in  $50^\circ$  steps for 60 minutes each. These heat treatments were carried out in a quartz furnace in a helium atmosphere.

After each step of annealing, a complete measurement of the angular variation of the EPR spectrum at room temperature was made, using intervals of  $2.5^\circ$  for critical runs and  $10^\circ$  otherwise. The microwave Q remained high through steps 0 to 17 ( $400^\circ\text{C}$ ), indicating that the Fermi level remained in the middle of the gap, as expected from previous work. The Q decreased somewhat after step 18 ( $450^\circ\text{C}$ ), and quite appreciably after step 19 ( $500^\circ\text{C}$ ), at which point only unanalysable traces of resonance remained. The centers formed at or below  $400^\circ\text{C}$  are thus characteristic of intrinsic material, but the Fermi level after the  $450^\circ$  anneal is uncertain. A measurement of its final Fermi level is under way.

#### Growth and Decay Curve:

Some 12 to 14 centers are observed to grow and decay during annealing. Fig. 6 plots the concentration of those centers for which g-tensors have been worked out and which can therefore be positively identified. As discussed below, the curves for a single center are internally consistent to  $\pm 15\%$ , while the relative and absolute concentrations are uncertain by factors of 2 or 3 either way.

These curves clarify the relations among the previously identified centers (N, I-III) and also the relation between Oak Ridge ( $T \sim 50^\circ\text{C}$ ) and Argonne ( $T \sim 100^\circ\text{C}$ ) irradiated samples. Center I was originally observed in Argonne irradiated material containing arsenic (Sample #1<sup>1</sup>); it is now found in pure crucible grown material irradiated at the lower temperature and annealed at  $300$  to  $350^\circ\text{C}$ . In fact, having determined the g-tensors for centers I', V, and VI, we have now identified all the important lines in the Argonne sample and find that their relative intensities correspond roughly to the  $300^\circ\text{C}$  step of annealing.

A striking feature of the annealing curves shown in Fig. 6 is the occurrence of pairs of centers which grow and decay together, and whose g-tensors show marked simi-



larities, as discussed later. The pairing of centers V and VI, for example, can hardly be coincidental, but no detailed explanation is yet available.

In these complicated spectra, lines overlap more often than not. Using the angular variation plots for each run, all the lines which appear (accidentally) to be in the clear at each angle are picked out for measurement, giving 15 and 40 intensity measurements for each center and temperature. These data are used to confirm the g-tensor assignments and to estimate defect concentrations. The accuracy of these estimates is discussed below.

(a) Confirmation of g-tensors: Each  $\langle 110 \rangle$  type center is represented by seven branches in the angular variation plot. To verify that the branches assigned to a given center do in fact grow and decay together, separate annealing curves were constructed for each branch. For a given run the branches belonging to a single center showed a maximum spread of 2:1 in intensity, with an r.m.s. deviation of  $\sim 16\%$  from the mean. As several of the centers were followed over a 20:1 variation in concentration, the agreement is convincing. Taken with the very precise internal consistency criteria, this seems sufficient to confirm the g-tensor assignments. However, the possibility that pairs of g-tensors belong to a single center is mentioned below.

(b) Relative concentrations: The standard deviation of the mean intensity calculated for each center is  $\pm 5$  to  $10\%$ , and is less than the systematic variation of  $\pm 15\%$  seen in the curves for centers II and III below  $130^\circ\text{C}$ . This variation appears to result from small relative changes in the filling factors of standard and sample when the latter is replaced after each run. The annealing curve for a given center is thus self consistent to  $\pm 15$  or  $20\%$ .

Assuming similar line shapes (gaussian), the relative concentrations of two centers are given by:

$$\frac{n_1}{n_2} = \frac{A_1}{A_2} \times \left( \frac{\Delta H_1}{\Delta H_2} \right)^2,$$

where A is the amplitude and  $\Delta H$  the line width. The  $20\%$  uncertainty in  $\Delta H$  introduces an uncertainty of 1.4:1 in the concentrations. Further, the amplitude of the hyperfine satellites must be added to that of the principal line. This correction amounts to  $+ 50\%$  for Center II, but has not been applied as the h.f.s. of the other centers is as yet unknown. Relative concentrations are thus reliable only within a ratio of 2:1 unless the hyperfine structure can be assumed similar.

(c) Absolute concentrations: The absolute concentration scale is derived by comparison with the internal ruby standard using the relation

$$\frac{N_2}{V_2} = \frac{\eta_1}{\eta_2} \frac{\alpha_1}{\alpha_2} \left( \frac{\Delta H_2}{\Delta H_1} \right)^2 \cdot \frac{12A_2}{A_1} \cdot \frac{N_1}{V_2}$$

$$= 1.24 \times 10^{15} (\Delta H_2)^2 \frac{A_2}{A_1}$$

The subscripts 1 and 2 refer to ruby and the sample, respectively, while the various quantities are defined as follows:

$$\frac{\eta_1}{\eta_2} = \frac{\langle H_{rf}^2 \rangle_1}{\langle H_{rf}^2 \rangle_2} = 0.216$$

$$\left( \frac{\alpha_1}{\alpha_2} \right) = \text{transition probability ratio} \sim 4$$

$$\Delta H_2 = \text{line width of ruby} = 15.9 \text{ gauss}$$

$$N_1 = \text{number of Cr}^{+++} \text{ spins in the Ruby standard} \sim 2.1 \times 10^{16}$$

$$V_1 = \text{sample volume} = 4.12 \times 10^{-2} \text{ cc.}$$

$$\frac{A_2}{A_1} = \text{amplitude ratio}$$

$N_1$  is estimated from the nominal 0.1%  $\text{Cr}^{+++}$  concentration in the ruby and may be in error by a factor of 2. Until a calibration of the standard is completed, the absolute concentrations are uncertain to a factor of 3 or 4:1.

#### g-tensors

The g-tensors and other properties of the centers discussed above are collected in Table 1. The tabulated values replace those given in the last report<sup>2</sup>; in particular, improved values for Center I have been obtained from the new data, while the N center g-tensor has been converted to absolute values consistent with the rest of the table. Center IV has not been identified with certainty in this sample, but is included for completeness. With the exception of IV, VII, and VIII, all the centers listed have been observed in at least two independent samples. Centers II, III, and N appear in floating zone material; the oxygen dependence of the others is unknown at present.

To obtain these g-tensors, a  $\cos \{ 2(\theta - \theta_0) \}$  curve is fitted to each branch of the angular variation plot to determine adjusted values for the nine different g-values belonging to the three principal directions. Four of these values are used to

compute the g-tensor; the remainder are subjected to consistency checks. The resulting g-tensors, in general, fit the data to  $\pm 0.5$  gauss, or within half a line width. A simplified least squares treatment is being performed to improve the g-tensors; the adjustments are not expected to exceed the quoted uncertainties of .0002 in g and  $0.2^\circ$  in  $\theta$ . The g-value scale is derived from simultaneous measurements (with the same counter) of the microwave frequency and the proton precession frequency, and is free of systematic error other than that introduced by our use of the published<sup>3</sup> ratio

$$\frac{\mu_o}{\mu_p} \approx 657.4758,$$

which is valid for protons in mineral oil, whereas our proton probe uses glycerine.

#### Discussion:

Fig. 1 shows a striking tendency of the damage centers to occur in pairs (II and III, V and VI, I and I', VII and VIII) which grow and anneal together. Examination of the tabulated g-tensors shows a general similarity between members of a pair; this similarity is rather more striking when the angular variation plots are examined. As this report is written we speculate that either the pairs represent two configurations of the same basic center, or that the two g-tensors actually represent the  $m_s = -1 \rightarrow m_s = 0$  and  $m_s = 0 \rightarrow m_s = +1$  transitions of the same  $S = 1$  system. We have not yet had time to test these possibilities.

In addition to the centers tabulated, at least two more are present in the annealing stages near  $170^\circ\text{C}$ , and one or two more in the  $450^\circ\text{C}$  stage. They are heavily obscured and it remains to be seen whether further analysis will disentangle them.

Several questions for future investigation are raised by these results. Foremost, perhaps, is the determination of the hyperfine structures in order to obtain information bearing on the microscopic structures. Also, however, there is the question of oxygen dependence; the rapid and complex phenomena in the  $450^\circ\text{C}$  region suggest a connection with the coagulation of oxygen impurity and require more detailed investigation. We have, however, abandoned the investigation of reaction kinetics suggested in the last report: the system appears far too complex.

TABLE I

Center	$\sim T^{\circ}\text{C}$ forms	$\sim T^{\circ}\text{C}$ anneals	$g_1$ (a) $\pm .0002$	$g_2$ $\pm .0002$	$g_3$ $\pm .0002$	$\theta$ $\pm 0.2^{\circ}$	$\Delta H$ (b) $\pm 0.2$ g.	Impurity dependence
II	?	$180^{\circ}$	2.0109	2.0127	1.9974	$14.9^{\circ}$	1.2	independent
III	?	$180^{\circ}$	2.0010	2.0072	2.0128	$32^{\circ}$	1.2	"
N	$150^{\circ}$	$500^{\circ}$	2.0089	2.0125	2.0045	$18.7^{\circ}$	1.2	"
I	$250^{\circ}$	$400^{\circ}$	2.0194	2.0243	1.9785	$12.8^{\circ}$	2.4	independent or Oxygen
I'	$250^{\circ}$	$400^{\circ}$	1.9971	1.9942	2.0305	$2.8^{\circ}$	2.4	
V	$250^{\circ}$	$450^{\circ}$	2.0125	2.0139	1.9940	$4.7^{\circ}$	1.2	"
VI	$250^{\circ}$	$450^{\circ}$	2.0015	2.0041	2.0148	$8.0^{\circ}$	1.2	"
VII	$300^{\circ}$	$500^{\circ}$	2.0127	2.0149	1.9937	$0^{\circ}$	1.6	"
VIII	$300^{\circ}$	$500^{\circ}$	2.0017	2.0031	2.0167	$0^{\circ}$	1.6	"
IV	$400^{\circ}?$	$500^{\circ}$	2.0088	2.0113	2.0050	$22.0^{\circ}$	1.1	"

(a)  $g_2$  is along  $\langle 110 \rangle$ ;  $g_1$  lies in the plane containing  $\langle 001 \rangle$  and  $\langle 110 \rangle$ , making an angle  $\theta$  with  $\langle 001 \rangle$ .

(b)  $\Delta H$  = full width between inflections, in gauss.

1. The samples used in this work are described in a previous report: Jung and Newell, Semiconductor Research, 3rd quarterly report, April 1 to June 30, 1961, p. 13.
2. Jung and Newell, Semiconductor Research, Final Report, Oct. 1, 1960 to Sept. 30, 1961, p. 10.
3. Cohen, Du Mont, et al., Rev. Mod. Phys. 27, 363 (1955).

# ELECTRON PARAMAGNETIC RESONANCE - GERMANIUM

D. Trueblood and G. Newell

## I. Apparatus

Construction of the x-band superheterodyne spectrometer is continuing. The microwave circuit and the klystron control circuits are complete and operate satisfactorily. Amplifiers and demodulators for the signal channel have been completed and are undergoing test.

## II. Filling Factor Calculations:

As mentioned in the last report, measurements will be made on cylindrical germanium samples located on the axis of a silicon filled  $TE_{011}$  mode cylindrical cavity. The configuration is sketched in Fig. 7, which also gives calculated curves of filling factor and cavity Q as a function of sample diameter. These curves serve to determine the optimum diameter for a sample of given conductivity. They supplement the results previously given for rectangular cavities<sup>1</sup>. The derivation of the expressions valid for small sample diameters is sketched below.

The rf field configuration in the cavity for  $r \leq a$  is given by:

$$\begin{aligned} E_{\theta} &= -J'_0 \left( \frac{2X_{01} k_{Ge} r}{D_0} \right) \sin \frac{2\pi z}{\lambda_g} \\ H_r &= \frac{\lambda_0}{\lambda_g} J'_0 \left( \frac{2X_{01} k_{Ge} r}{D_0} \right) \cos \frac{2\pi z}{\lambda_g} \\ H_z &= \frac{X_{01} \lambda_0 k_{Ge}}{\pi D_0} J_0 \left( \frac{2X_{01} k_{Ge} r}{D_0} \right) \sin \frac{2\pi z}{\lambda_g} \end{aligned}$$

and for  $r \geq a$  is given by:

$$\begin{aligned} E_{\theta} &= -A_0 J'_0 \left[ \frac{2X_{01} k_{si}}{D_0} \left( r + \frac{D_0}{2k_{si}} - \frac{D}{2} \right) \right] \sin \frac{2\pi z}{\lambda_g} \\ H_r &= A_0 \frac{\lambda_0}{\lambda_g} J'_0 \left[ \frac{2X_{01} k_{si}}{D_0} \left( r + \frac{D_0}{2k_{si}} - \frac{D}{2} \right) \right] \cos \frac{2\pi z}{\lambda_g} \\ H_z &= A_0 \frac{X_{01} \lambda_0 k_{si}}{\pi D_0} J_0 \left[ \frac{2X_{01} k_{si}}{D_0} \left( r + \frac{D_0}{2k_{si}} - \frac{D}{2} \right) \right] \sin \frac{2\pi z}{\lambda_g} \end{aligned}$$

where  $a$  is the radius of the Ge sample,  $X_{01} = 3.832$  for a  $TE_{01}$  mode,  $D_o$  is diameter of an air filled cavity,  $k$  is the dielectric constant,  $A_o$  is an amplitude factor,  $\lambda_o$  is free space wavelength,  $\lambda_g$  is the guide wavelength, and  $D$  the loaded cavity diameter.

$A_o$  and  $D$  were calculated as functions of  $a$  by matching  $E_{tan}$  and  $H$  across the boundary  $r = a$ .  $\lambda_g$  also depends on  $a$ , but for small values of  $a$  both  $D$  and  $\lambda_g$  approximately equal the values for a Si filled cavity.

The filling factor integral

$$n = \frac{\int_{\text{samp.}} H_{rf}^2 dv}{\int_{\text{cav.}} H_{rf}^2 dv}$$

was evaluated using the Bessel integral expression

$$\int_0^c r [J_n(\lambda r)]^2 dr = \frac{c^2}{2} \{ [J_n(\lambda c)]^2 + [J_{n+1}(\lambda c)]^2 \} - \frac{n c}{\lambda} J_n(\lambda c) J_{n+1}(\lambda c)$$

and the Bessel expansion to 2nd order for small  $a$ .

The result, accurate for

$$\frac{2X_{01} k a}{D_o} \lesssim 1$$

is

$$n = \frac{P + Q}{P + Q + R + S}$$

where

$$\begin{aligned} P &= \left( \frac{\lambda_o}{\lambda_g} \right)^2 \left( \frac{a^2}{8} \right) \left( \frac{2X_{01} k_{Ge} a}{D_o} \right)^2 \\ Q &= \left( \frac{X_{01} \lambda_o k_{Ge}}{\pi D_o} \right)^2 \left( \frac{a^2}{2} \right) \left[ 1 - \frac{1}{4} \left( \frac{2X_{01} k_{Ge} a}{D_o} \right)^2 \right] \\ R &= \left( A_o \frac{\lambda_o}{\lambda_g} \right)^2 \left[ \frac{D_o^2}{8} [J_2(X_{01})]^2 - \frac{a^2}{8} \left( \frac{2X_{01} k_{Si} a}{D_o} \right)^2 \right] \\ S &= \left( A_o \frac{X_{01} \lambda_o k_{Si}}{\pi D_o} \right)^2 \left\{ \frac{D_o^2}{8} [J_0(X_{01})]^2 - \frac{a^2}{2} \left[ 1 - \frac{1}{4} \left( \frac{2X_{01} k_{Si} a}{D_o} \right)^2 \right] \right\} \end{aligned}$$

The equation used to estimate the loading due to Ge is

$$Q_1 = \frac{\epsilon_0 \omega \int_{\text{cav.}} E_{\text{rf}}^2 dv}{\int_{\text{samp.}} \sigma_{\text{Ge}} E_{\text{rf}}^2 dv}$$

where  $\sigma_{\text{Ge}}$  is the Ge conductivity and is assumed independent of E so that we may remove it from the integral. Further,  $\sigma_{\text{Ge}}$  is assumed small enough so as not to affect the field configuration. The calculation is similar to that of n and both results are plotted in Fig. 7. For  $\lambda_0 = 3.19$  cm ( $f = 9.4$  kmc) we have  $D \approx 1.20$  cm.  $k_{\text{Si}}$  and  $k_{\text{Ge}}$  are taken to be 11.8 and 16 respectively.

The unloaded Q of the cavity is  $Q_0 \approx 8700$  and  $Q_0$  and  $Q_1$  are added in parallel to obtain the loaded Q. In view of the low conductivity of intrinsic Ge at room temp, it will be necessary to use a small sample and low temperatures to maintain a reasonable Q. The reduction in n, of course, puts a lower limit on sample radius.

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1. Nisenoff and Fan, Semiconductor Research, Fifteenth Quarterly Report, Feb. 1, 1960 to April 30, 1960.

## OPTICAL BEHAVIOUR OF IRRADIATED SILICON

A. K. Ramdas and H. Y. Fan

Our previous work<sup>1</sup> has shown that the two infrared absorption bands at 11.98 microns and 11.56 microns, produced in silicon by neutron or electron irradiation, are associated with the presence of oxygen in the material. The previous study of the growth of these absorption bands with 4.5 Mev electron irradiation indicated that the 11.98 micron band grew at about the same rate but saturated at a lower level with irradiation at liquid nitrogen temperature as compared with irradiation at 0°K. Such behavior was difficult to explain on a simple basis. However, the low temperature cell used in the experiment was not suitable for accurate optical measurement, and the indication for the saturation behavior was given by only one point in the curve.

The irradiation at liquid nitrogen temperature has been repeated with a low temperature cell of better design. As was found in the previous measurement, the 11.98 micron band grew at first linearly with electron flux, at about the same rate as with 0°K irradiation. Furthermore, the band did not saturate at a lower level as

indicated in the previous measurement but tended to saturate in the same manner as with 0°K saturation. Thus there is no appreciable difference between the two temperatures with regard to the production of the 11.98 micron absorption band (See Fig. 8).

In agreement with the previous measurement, the 11.56 micron band was not observed during the liquid nitrogen irradiation. The band was observed after the sample had been warmed up to room temperature. Irradiation at liquid helium temperature is planned in order to ascertain whether the formation of the 11.98 micron band is inhibited at sufficiently low temperature.

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1. A. K. Ramdas and H. Y. Fan - Semiconductor Research, First Quarterly Report, October 1, 1960 to December 31, 1960.



### III. LOW TEMPERATURE STUDIES

#### SPECIFIC HEAT MEASUREMENTS OF INDIUM WITH SMALL PERCENTAGES OF IMPURITY

P. H. Keesom and B. J. L. van der Hoeven, Jr.

Last year Bryant and one of us<sup>1</sup> found that the specific heat of superconductive indium between 0.4°K and 0.7°K was less than the lattice contribution in the normal state.

Ferrel<sup>2</sup> proposed an explanation of this specific heat anomaly which is based on an anomalous dispersion in the phonon spectrum. The interaction between phonons and electrons leads to a self energy of the phonons, due to creation and reabsorption of electron-hole pairs. The energy gap in the electronic states of the superconductor prevents the creation of electron-hole pairs for phonons with too small an energy, and, consequently, the self energy term disappears for a certain range of phonon frequencies. This leads to a lowering of the frequencies of the phonons in the superconductive state, relative to the phonons in the normal state. As a consequence, a new term, equal to  $-BT^2$ , is obtained in the specific heat of the superconductor.

A distinct advantage of this theory is that it predicts the effect for indium, but not for tin, since it depends on the coupling between phonons and electrons.

As one of the experimental tests, Ferrell indicates that for phonons with wavelengths longer than the coherence length, this effect should disappear. The coherence length is a measure of the extension of the electron wave packet taking part in the superconductive phenomena. His idea is that for phonon wavelengths longer than the coherence length, we expect the normal bulk elastic constants to give a correct description of the sound waves, and thus, also the normal lattice specific heat. From the work of Pippard<sup>3</sup>, Ferrell deduces that if a metal (such as indium) showing the heat anomaly were heavily enough doped with an alloying impurity to reduce significantly the coherence length, then the anomaly would disappear.

Measurements on indium doped with tin are now in progress.

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1. C. A. Bryant and P. H. Keesom, Phys. Rev. 123, No. 2, 491 (1961).
  2. R. A. Ferrell, Phys. Rev. Letters 6, No. 10, 541 (1961).
  3. A. B. Pippard, Phil. Mag. 46, 1104 (1955).

## PIEZO-THERMAL CONDUCTIVITY IN GERMANIUM

R. J. Sladek

The thermal conductivity of degenerate n-type germanium (containing  $2 \times 10^{17}$  Sb atoms/cc) has been measured between 1.5°K and 4.1°K with tensile stresses from zero to  $1.5 \times 10^8$  dynes/cm<sup>2</sup> applied in the [110] crystallographic direction. Fig. 9 shows the temperature dependence of the thermal conductivity with no applied stress and with  $1.0 \times 10^8$  dynes/cm<sup>2</sup> applied. For all temperatures, this applied stress increases the thermal conductivity only slightly (about 10%). This is in sharp contrast to the behavior of germanium more lightly doped with Sb for which large increases in the thermal conductivity can be obtained at the lower temperatures<sup>1</sup>. A detailed comparison of these effects is given in Fig. 10 which shows that the ratio of unstressed to stressed thermal conductivity is independent of temperature for the degenerate sample while this ratio decreases strongly with decreasing temperature for the more lightly doped sample (data on the latter from reference 1).

The relatively small piezo-thermal conductivity effect in the degenerate sample can be explained qualitatively by noting that in such a sample the donor levels have merged with the conduction band and the donors are ionized even at the lowest temperatures. Consequently, the strongly stress-dependent scattering of phonons by bound donor electrons<sup>1</sup> is absent.

The different temperature dependences of the piezo-thermal conductivity for the degenerate and non-degenerate samples also suggest that the mechanisms by which electrons scatter phonons are different in these two types of materials.

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1. R. W. Keyes and R. J. Sladek, Phys. Rev. (Jan. 15, 1962).

## GERMANIUM RESISTANCE THERMOMETERS

N. Pearlman and M. P. Mathur

In the measurements described in earlier Progress Reports, it was found that the reproducibility of the thermometers in successive runs was rather good, provided that relative values  $R(T)/R_0$  were compared, where  $R_0$  is the resistance at an arbitrary temperature (usually  $R_0 = R(4^\circ\text{K})$ ). However,  $R(T)$  itself was usually reproducible only to such an extent that a given resistance value might correspond, on different runs, to temperatures differing by as much as  $\Delta T \sim 0.1^\circ\text{K}$ .

Part of these differences could be accounted for, on runs between which leads had been resoldered to the thermometer, by the possibility that melting of the solder attaching the heavy leads to the thermometer had changed the effective sample dimensions between leads. To avoid this, the heavy leads were attached to the thermometer with tin-lead solder while the thin wires were attached to the heavy leads with low-melting cerroseal solder.

Another possible factor affecting reproducibility could be strain in the thermometer due to differential thermal contraction between the thermometer and the base on which it is mounted, or the adhesive bonding it to the base. The former is apparently not too important, since thermometers mounted on a Ge base did not behave differently from those measured earlier, mounted on a copper base. In order to eliminate the latter influence thermometers were made in the "L" shape shown in Fig. 11 and mounted on the short leg. With this configuration, reproducibility on successive runs becomes a few millidegrees. The thermal contact resistance  $dT/dP$  between thermometer and base, where  $P$  is power dissipated in the thermometer, is about the same as that for the earlier thermometers, roughly a millidegree per microwatt, which is about two orders of magnitude smaller than that reported for encapsulated Ge thermometers by Lindenfeld<sup>1</sup>.

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1. P. Lindenfeld, Rev. Sci. Inst. 32, 9 (1961).

#### IV. GENERAL

##### SHALLOW ACCEPTOR STATES IN GERMANIUM

H. M. James and K. S. Mendelson

Solutions of the effective mass equations for shallow acceptors in germanium have been obtained using a variational method in which the angular dependence of the trial function was determined from symmetry considerations<sup>1</sup> and the radial dependence was determined by the variational calculation.

Let  $J_x, J_y, J_z$  be matrices corresponding to components of angular momentum 3/2. Let

$$\{J_\alpha J_\beta\} = \frac{1}{2} (J_\alpha J_\beta + J_\beta J_\alpha).$$

Then the effective mass Hamiltonian for acceptors in germanium can be written

$$\begin{aligned} H = & -\frac{\hbar^2}{2m} \left( \gamma_1 + \frac{5}{2} \gamma_2 \right) \nabla^2 + \frac{\hbar^2}{m} \gamma_2 \left( J_x^2 \frac{\partial^2}{\partial x^2} + J_y^2 \frac{\partial^2}{\partial y^2} + J_z^2 \frac{\partial^2}{\partial z^2} \right) \\ & + \frac{2\hbar^2}{m} \gamma_3 \left[ \{J_x J_y\} \frac{\partial^2}{\partial x \partial y} + \{J_y J_z\} \frac{\partial^2}{\partial y \partial z} + \{J_z J_x\} \frac{\partial^2}{\partial z \partial x} \right] - \frac{e^2}{K r}. \end{aligned} \quad (1)$$

where  $\gamma_1, \gamma_2, \gamma_3$  are constants which can be determined from cyclotron resonance experiments<sup>2,3</sup>. The energy has been chosen to be positive in the direction of increasing hole energy; thus the bound state energies of the acceptor will be negative.

The ground state wave functions transform according to the  $\Gamma_8$  irreducible representation of the double tetrahedral group. The function

$$\psi = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} f_1(r) + \begin{bmatrix} z^2 - \frac{1}{2}(x^2 + y^2) \\ 0 \\ -\frac{3}{2}(x^2 - y^2) \\ 0 \end{bmatrix} f_2(r) + i \begin{bmatrix} 0 \\ x + iy \\ xy \\ 0 \end{bmatrix} f_3(r), \quad (2)$$

having this transformation property, was used as a trial function<sup>1</sup>. The first term has s-like dependence on angle, and the others have d-like dependence. (Factors of  $r^2$  were included in the d-like angular terms for convenience in calculation.)

Extremalizing the functional

$$L = \int \psi^* (H - E) \psi d^3x$$

with respect to variations of the  $f$ 's leads to a system of ordinary differential equations for the  $f$ 's. It is convenient to define

$$\begin{aligned} g_1 &= r f_1, \\ g_2 &= r^3 f_2, \\ g_3 &= r^3 f_3. \end{aligned}$$

The differential equations for the  $g$ 's are then

$$g_1'' + \left(\epsilon + \frac{2}{r}\right) g_1 - \frac{4\gamma_2}{5\gamma_1} (g_2'' + \frac{3}{r} g_2') + \frac{2\sqrt{3}\gamma_3}{5\gamma_1} (g_3'' + \frac{3}{r} g_3') = 0, \quad (3a)$$

$$-\frac{2\gamma_2}{\gamma_1} (g_1'' - \frac{3}{r} g_1' + \frac{3}{2} g_1) + g_2'' + \left(\epsilon + \frac{2}{r} - \frac{6}{r^2}\right) g_2 = 0, \quad (3b)$$

$$\frac{2\sqrt{3}\gamma_3}{\gamma_1} (g_1'' - \frac{3}{r} g_1' + \frac{3}{2} g_1) + g_3'' + \left(\epsilon + \frac{2}{r} - \frac{6}{r^2}\right) g_3 = 0, \quad (3c)$$

Here we have used as units of energy and length

$$\begin{aligned} \epsilon_0 &= \frac{m e^4}{2 K^2 h^2 \gamma_1} = 0.00403 \text{ ev}, \\ L_0 &= \frac{K h^2 \gamma_1}{m e^2} = 110 \text{ \AA}. \end{aligned}$$

The functions  $g_i$  must satisfy the boundary conditions

$$g_i \rightarrow 0 \text{ as } r \rightarrow 0, r \rightarrow \infty \quad (i = 1, 2, 3).$$

We first observe that these equations have solutions with  $g_1 \equiv 0$  and  $g_2, g_3$  satisfying

$$\begin{aligned} g_2'' + \left(\epsilon + \frac{2}{r} - \frac{6}{r^2}\right) g_2 &= 0, \\ g_3 &= \frac{2\gamma_2}{\sqrt{3}\gamma_3} g_2. \end{aligned}$$

This equation for  $g_2$  is simply the equation for hydrogenic radial functions with  $l = 2$ . It will have acceptable solutions for  $\epsilon = -1/n^2$ ,  $n = 3, 4, 5, \dots$ . These solutions, however, do not give an approximation to the ground state function. The lowest energy,  $\epsilon = -1/9$ ,  $E = -0.00045$  ev, is much higher than the experimental ground state energies<sup>4</sup> of  $-0.010$  to  $-0.014$  ev.

If  $g_1 \neq 0$ , we can eliminate it from Eqs. (3a) and (3b). This gives

$$\frac{d^2}{dr^2} (\sqrt{3} \gamma_3 g_2 + \gamma_2 g_3) + \left( \epsilon + \frac{2}{r} - \frac{6}{r^2} \right) (\sqrt{3} \gamma_3 g_2 + \gamma_2 g_3) = 0.$$

This is again the hydrogenic radial equation. There will be acceptable, non-trivial solutions for  $\sqrt{3} \gamma_3 g_2 + \gamma_2 g_3$  only when  $\epsilon = -1/n^2$ . As we have seen, these solutions will not be approximations to the ground state functions. Thus for the ground state we must have

$$g_3 = - \frac{\sqrt{3} \gamma_3}{\gamma_2} g_2.$$

Elimination of  $g_3$  from Eqs. (3) gives

$$g_1'' + \left( \epsilon + \frac{2}{r} \right) g_1 - A \left( g_2'' + \frac{3}{r} g_2' \right) = 0, \quad (4a)$$

$$- B \left( g_1'' - \frac{3}{r} g_1' + \frac{3}{r^2} g_1 \right) + g_2'' + \left( \epsilon + \frac{2}{r} - \frac{6}{r^2} \right) g_2 = 0, \quad (4b)$$

where

$$A = \frac{2 (2\gamma_2^2 + 3\gamma_3^2)}{5 \gamma_1 \gamma_2},$$

$$B = \frac{2\gamma_2}{\gamma_1}.$$

These equations cannot be solved analytically. We have therefore obtained numerical solutions using the Runge-Kutta method<sup>5</sup>.

To determine the initial conditions, one can try solutions of the form

$$\begin{aligned} g_1 &= r^{n_1} \sum_{\tau=0}^{\infty} a_{\tau} r^{\tau}, \\ g_2 &= r^{n_2} \sum_{\tau=0}^{\infty} b_{\tau} r^{\tau}. \end{aligned} \quad (5)$$

One finds that  $n_1 = n_2 = n = 3, 1, 0, -2$ . We note that the indices differ by integers. In this case, there will not be a solution of the form (5) for each value of  $n$ <sup>6</sup>. There will be a solution of the form (5) for  $n = 3$ . We denote this solution by

$$\begin{aligned} y_1 &= r^3 \sum_{\tau=0}^{\infty} a_{\tau} r^{\tau} \\ y_2 &= r^3 \sum_{\tau=0}^{\infty} b_{\tau} r^{\tau} \end{aligned} \quad (6)$$

In addition there will be a solution of the form<sup>6</sup>

$$\begin{aligned} z_1 &= y_1 \ln r + \bar{g}_1 \\ z_2 &= y_2 \ln r + \bar{g}_2 \end{aligned}$$

We denote this solution by

$$\begin{aligned} z_1 &= y_1 \ln r + r \sum_{\tau=0}^{\infty} c_{\tau} r^{\tau}, \\ z_2 &= y_2 \ln r + r^2 \sum_{\tau=0}^{\infty} d_{\tau} r^{\tau}. \end{aligned} \quad (7)$$

From the differential equations, one can derive recurrence relations for the coefficients  $a_{\tau}, b_{\tau}, c_{\tau}, d_{\tau}$ . There are two other linearly independent solutions of Eq. (4), but they do not behave acceptably as  $r \rightarrow 0$ .

It is also necessary to consider the asymptotic behavior as  $r \rightarrow \infty$ . There are four linearly independent asymptotic solutions that have the forms

$$\begin{aligned} g_1 &\sim ae^{\pm \alpha r}, & g_2 &\sim be^{\pm \alpha r} \\ \text{or} & & & \\ g_1 &\sim ae^{\pm \beta r} & g_2 &\sim -be^{\pm \beta r}. \end{aligned} \quad (\alpha > \beta) \quad (8)$$

As  $r \rightarrow \infty$ , the solution with  $e^{\alpha r}$  will blow up more rapidly than that with  $e^{\beta r}$ ; hence this will be called the dominant solution, and that with  $e^{\beta r}$  the sub-dominant solution.

For a given energy, one can use the solutions described by Eqs. (6) or (7), or any linear combinations of them, to determine  $g_1(r_0), g'_1(r_0), g_2(r_0), g'_2(r_0)$

( $r_0$  small) for a solution that is well-behaved as  $r \rightarrow 0$ . Starting from  $r_0$  with these initial values, one can integrate Eq. (4) numerically to obtain a solution that is well-behaved at the origin but will, in general, become infinite as  $r \rightarrow \infty$ . If an arbitrary linear combination of Eqs. (6) and (7) is used to obtain the initial conditions, the solution at large  $r$  will approach some linear combination of the dominant and sub-dominant solutions. In general, such a solution will blow up even if  $\epsilon$  is an eigenvalue of the problem. To obtain a solution that is well-behaved as  $r \rightarrow \infty$ , it is necessary to adjust not only the energy, but also the linear combination of Eqs. (6) and (7) that is used to obtain the initial conditions.

One can, for any  $\epsilon$ , choose the initial conditions so that only the sub-dominant term appears at large  $r$ . For an energy that is an eigenvalue, the sub-dominant term disappears also, and one obtains a solution that is well-behaved as  $r \rightarrow \infty$ . To eliminate the dominant solution, the following procedure was used. For each energy two solutions ( $g_1, g_2$ ) were determined, starting from initial conditions determined by Eqs. (6) and (7), respectively. It was found that the solution given by Eq. (6) had essentially pure dominant behavior at large  $r$ . We took the ratio  $g_1/g_2$  of this solution at large  $r$  to be  $a/b$  (Eq. (8)). Using the value of  $a/b$  obtained in this way, we chose a linear combination of the solutions such that the ratio  $g_1/g_2$  at the end of the range of integration (determined by practical considerations of computing time) was  $-a/b$ . The resulting curves gave essentially pure sub-dominant behavior at large  $r$ . The value of  $g_1$  at a point near the end of the range of integration, chosen so far out that a well-behaved solution would be negligible, was used as a measure of the amount of sub-dominant solution present. By repeating this process for several energies, it was possible to find eigenvalues and corresponding eigenfunctions.

Using this method, we determined the energy and radial functions for the ground state, and for the first excited state described by the trial function (2). We also applied a similar method to the  $\Gamma_7$  and  $\Gamma_6$  excited states<sup>1</sup>. For the  $\Gamma_7$  states, we used the trial function

$$\psi = \begin{bmatrix} x + iy \\ 0 \\ -3(x - iy) \\ 2iz \end{bmatrix} f_1(r) + \begin{bmatrix} -\frac{3}{4}[(z^2 - \frac{1}{5}r^2)(x + iy) + (x - iy)^3] \\ \frac{1}{2} \frac{3}{2} [z(x + iy)^2 + z(x - iy)^2] \\ -\frac{3}{4} [7(z^2 - \frac{1}{5}r^2)(x - iy) - (x + iy)^3] \\ -3rz(z^2 - \frac{3}{5}r^2) \end{bmatrix} f_2(r)$$

and for the  $\Gamma_6$  states we used the trial function



$$\psi = \begin{bmatrix} 3(x - iy) \\ 2iz \\ x + iy \\ 0 \end{bmatrix} f_1(r) + \begin{bmatrix} -\frac{3}{4} [7(z^2 - \frac{1}{5}r^2)(x - iy) - (x + iy)^3] \\ 3iz(s^2 - \frac{3}{5}r^2) \\ \frac{3}{4} [(z^2 - \frac{1}{5}r^2)(x + iy) + (x - iy)^3] \\ \frac{1}{2} [z(x + iy)^2 + z(x - iy)^2] \end{bmatrix} f_2(r)$$

Here there are only two terms in each trial function, and the variational procedure gave immediately two coupled differential equations for the  $f$ 's. These equations were solved numerically by the method described above. The energies thus found are shown in Table I, and the radial functions in Figs. 12 - 16. These results were obtained using the values of  $\gamma_1, \gamma_2, \gamma_3$  given in reference 3.

TABLE I. Eigenvalues of Effective Mass Hamiltonian for Shallow Acceptor States in Germanium.

Trial Function	Energy	
	$\epsilon_0$	$10^{-3} \text{ev}$
$\Gamma_8$	-2.32	-9.28
	-0.690	-2.76
$\Gamma_7$	-0.484	-1.94
	-0.250	-1.00
$\Gamma_6$	-0.146	-0.584

---

1. D. Schechter, Theory of Shallow Acceptor States in Silicon and Germanium. Ph.D. Thesis, Carnegie Institute of Technology, unpublished.
2. G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955).
3. B. W. Levinger and D. R. Frankl, J. Phys. Chem. Solids, 20, 281 (1961).
4. P. Fisher and H. Y. Fan, Phys. Rev. Letters 2, 456 (1959).
5. F. B. Hildebrand, "Introduction to Numerical Analysis" (McGraw Hill, New York, 1956) pp. 233-239.
6. E. L. Ince, "Ordinary Differential Equations" (Dover Publications Inc., New York, 1956) p. 160 and Sec. 15.311.

## GROWTH OF ZINC TELLURIDE SINGLE CRYSTALS FROM THE VAPOUR PHASE

P. H. Klose

Work has been started to prepare the compound semiconductor zinc telluride, ZnTe. Equimolecular parts of the chemically pure constituents are weighed, mechanically mixed, and melted together in a quartz tube. A purified hydrogen ambient is used to prevent oxidation during this process. Any excess metal is distilled away afterwards in a high vacuum furnace. The material so prepared is already quite dense and is in the shape of a rod. This rod is then placed in a furnace for the growing of the crystal. The furnace is essentially similar to that described by Polich and co-workers<sup>1</sup>. Experiments are being carried out to determine the optimum temperature profile of the growing furnace and the corresponding rate of growth in order to obtain single crystals. Measurements of Hall coefficient and resistivity of the material prepared have been made at room temperature. Hall mobilities of  $50 \text{ cm}^2/\text{volt-sec}$  have been found for samples with resistivities of the order of  $1 \Omega \text{ cm}$ .

---

1. Piper, Polich, J. A. P., 32, 1278 (1961).

## MATERIAL PREPARATION

K. Masumoto and L. Roth

Work has continued on the preparation of large crystals of ZnSb under various growth conditions using the Bridgman method. Attempts were made to obtain single crystals by the Czochralski technique using the Bridgman method crystals as seeds. So far, it has not been possible to obtain large single crystals without twinning. Improvements are being made in the crystal pulling apparatus with the aim of obtaining single crystals.

The usual work of making single crystals of Ge, InSb, and GaSb continues.

TRAVEL ON PRF 2641

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October 9, 1961  
To visit the Electronic Equipment  
Display at the National Electronics  
Conference.

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To attend the Midwest Solid State  
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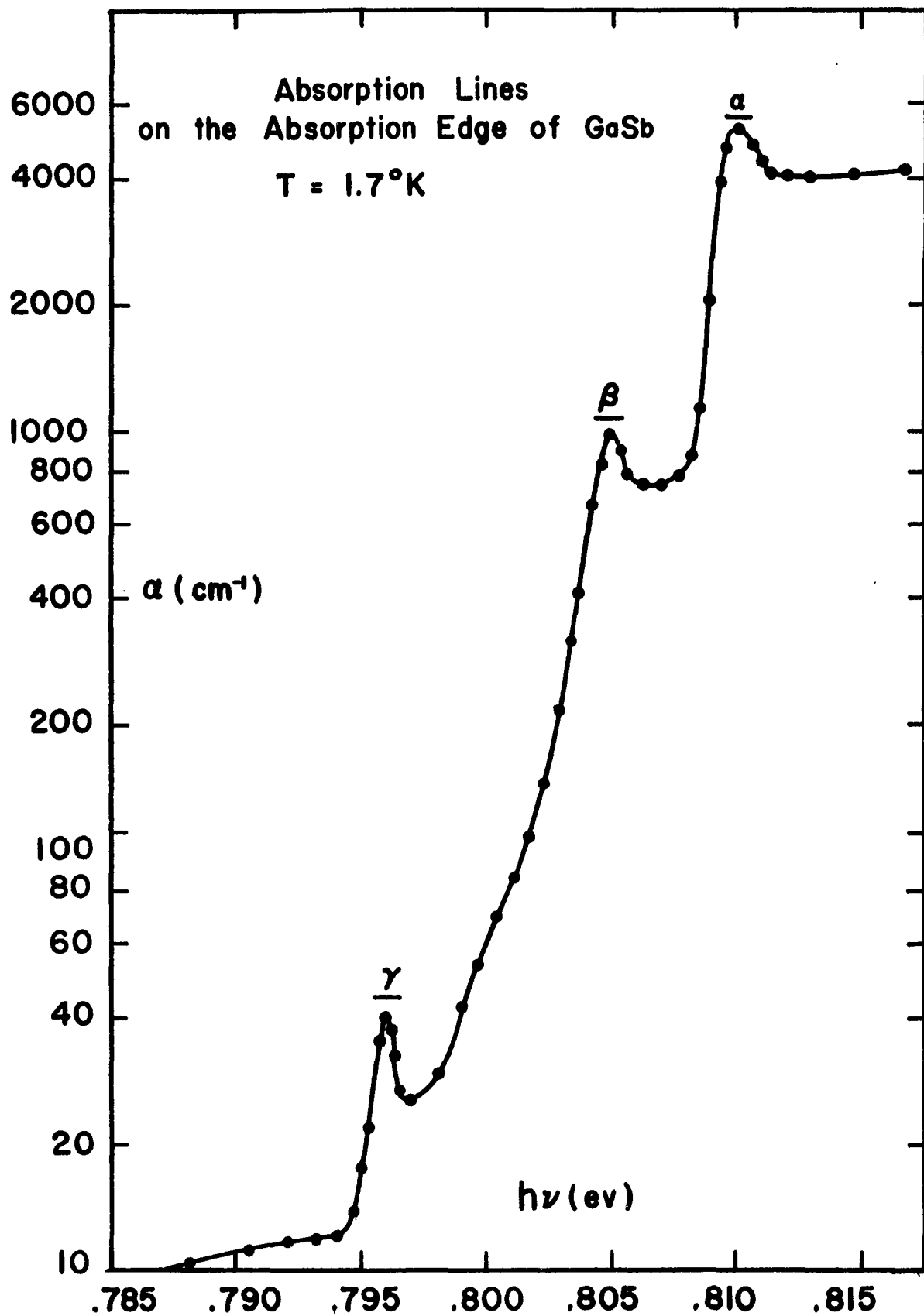


Fig. 1

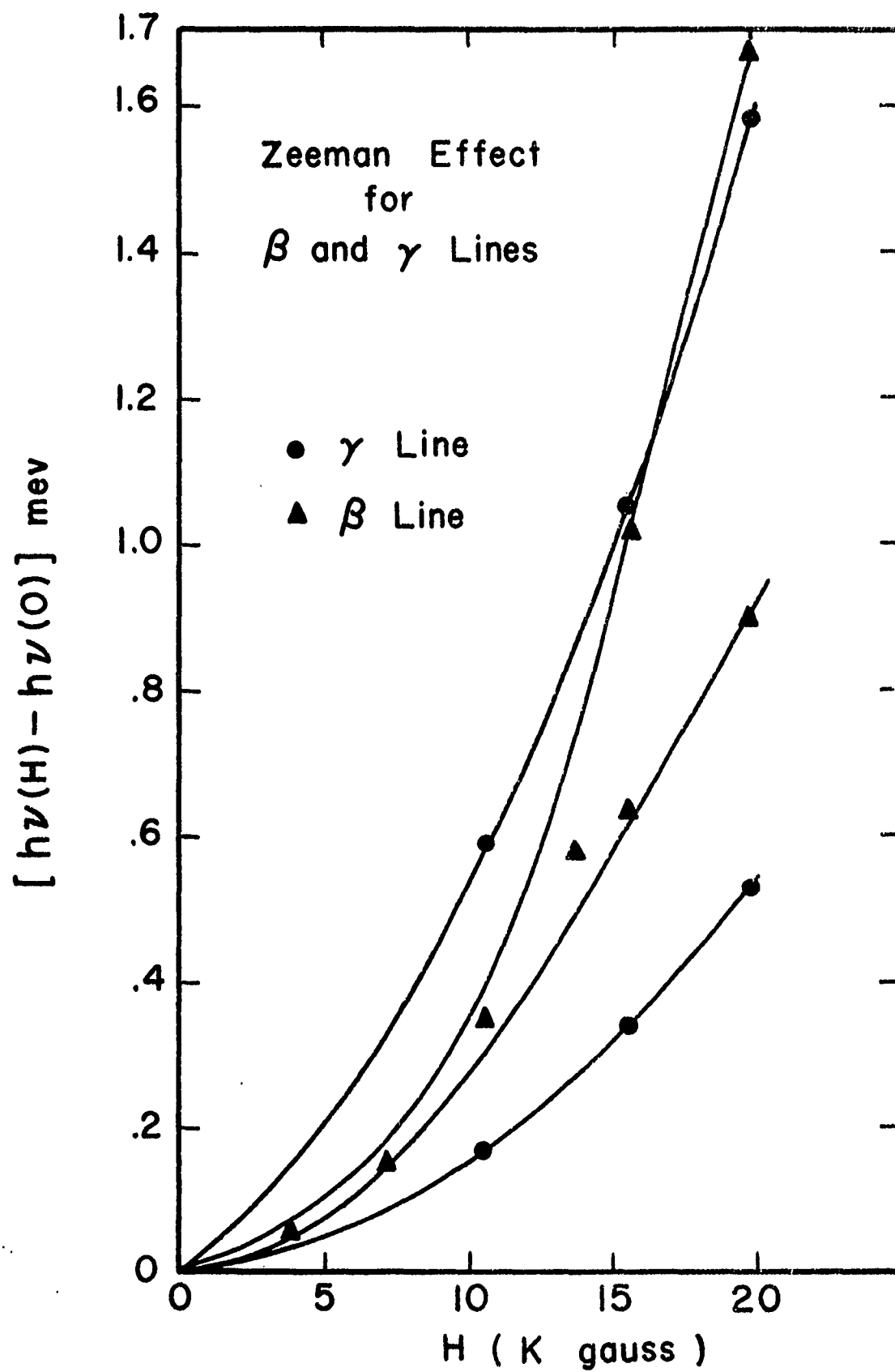
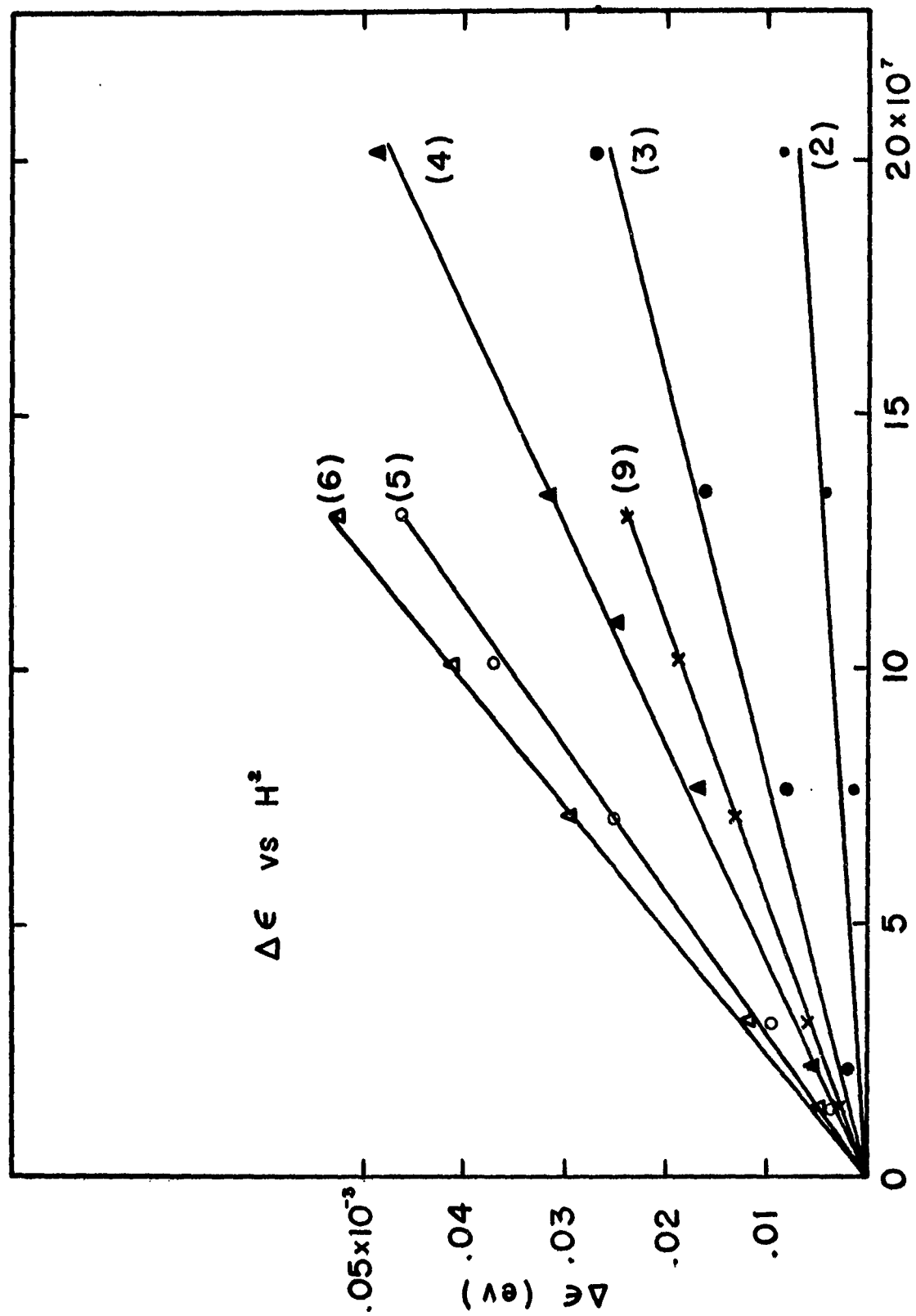


Fig. 2



$H^2$  (oe) $^2$

Fig. 3

# $TM_{110}$ MODE 5MM CAVITY AND COUPLING TO WAVEGUIDE

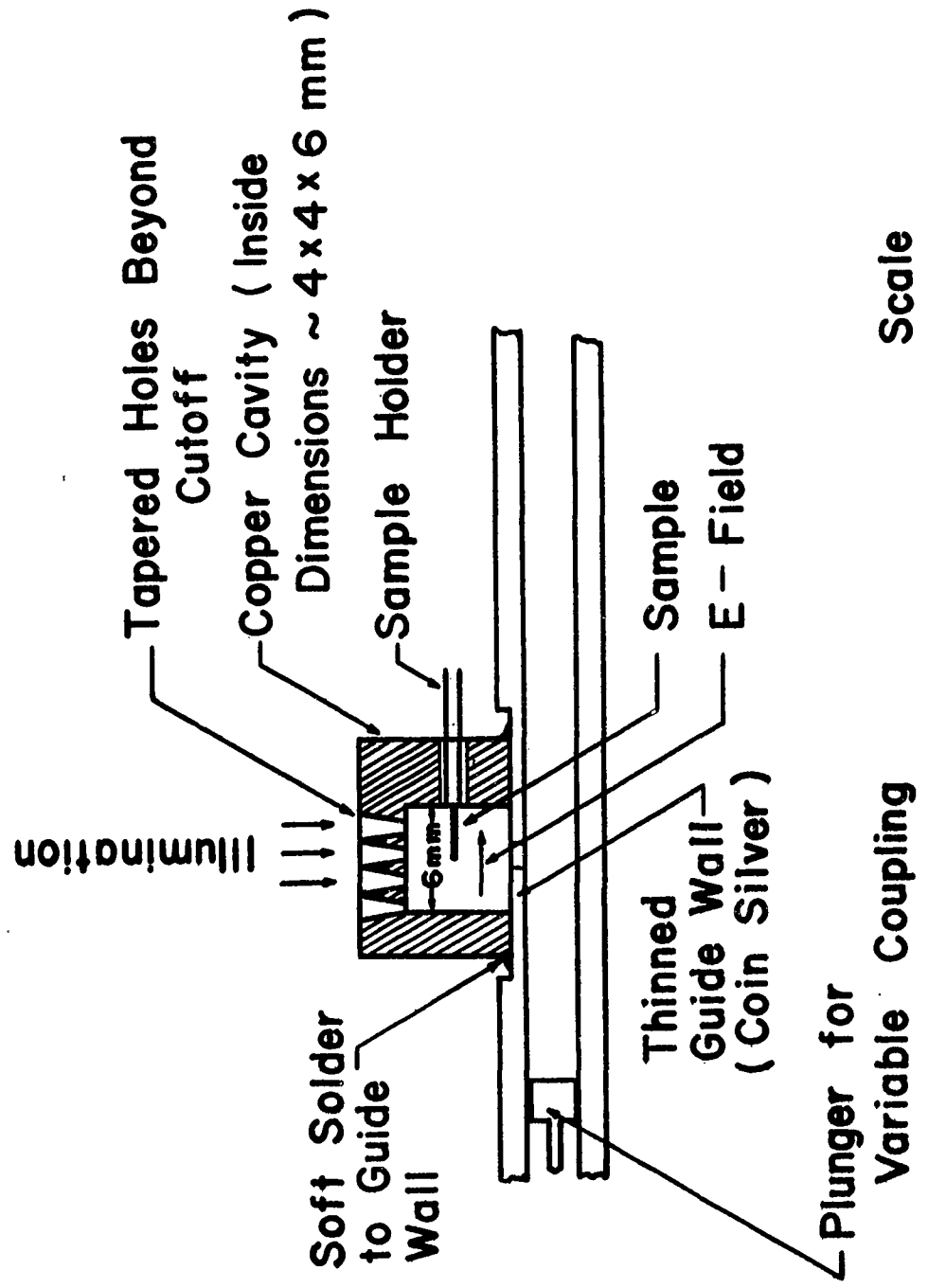


Fig. 4

Scale  
~ 1:4

# 5MM CYCLOTRON RESONANCE APPARATUS

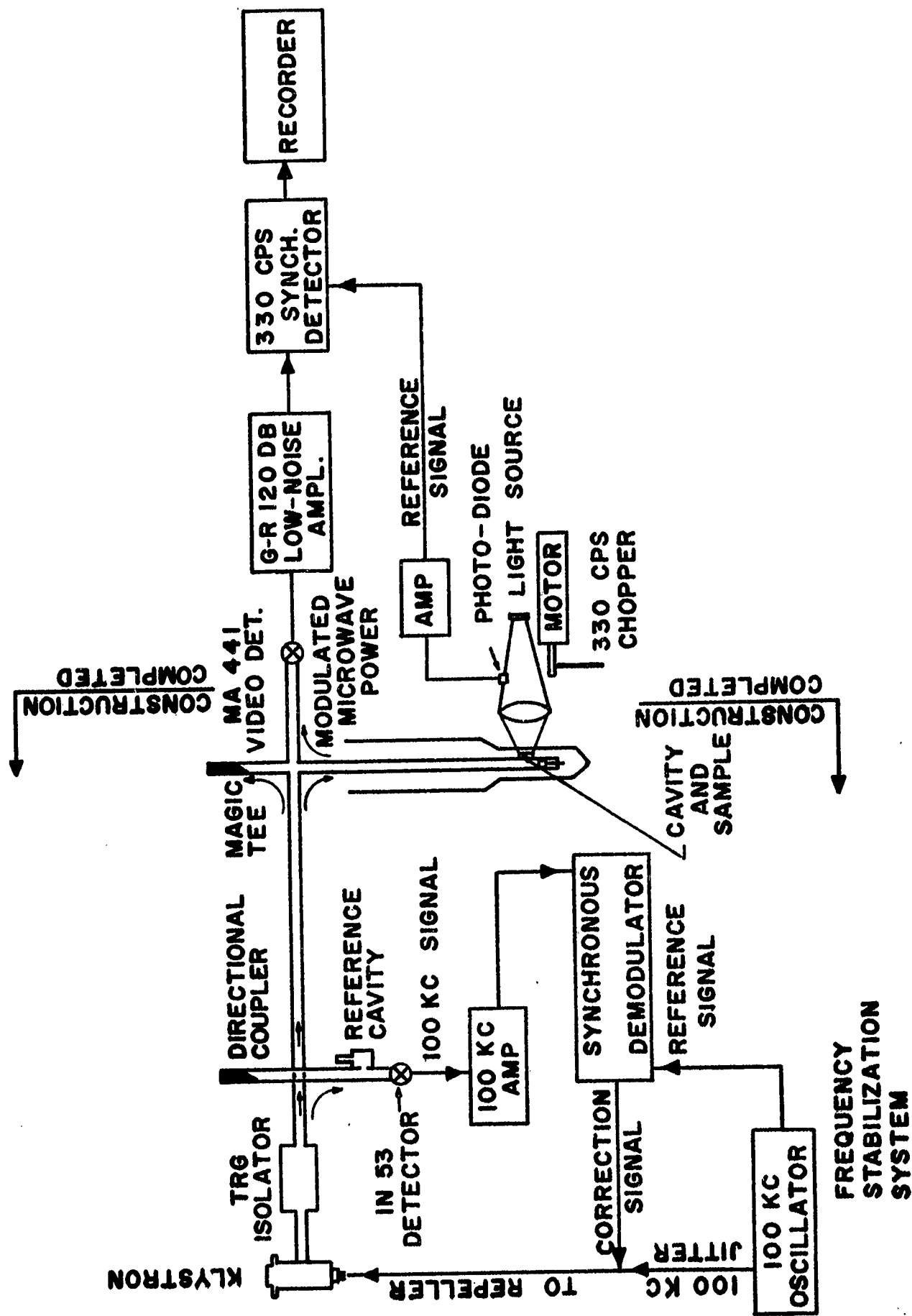


Fig. 5



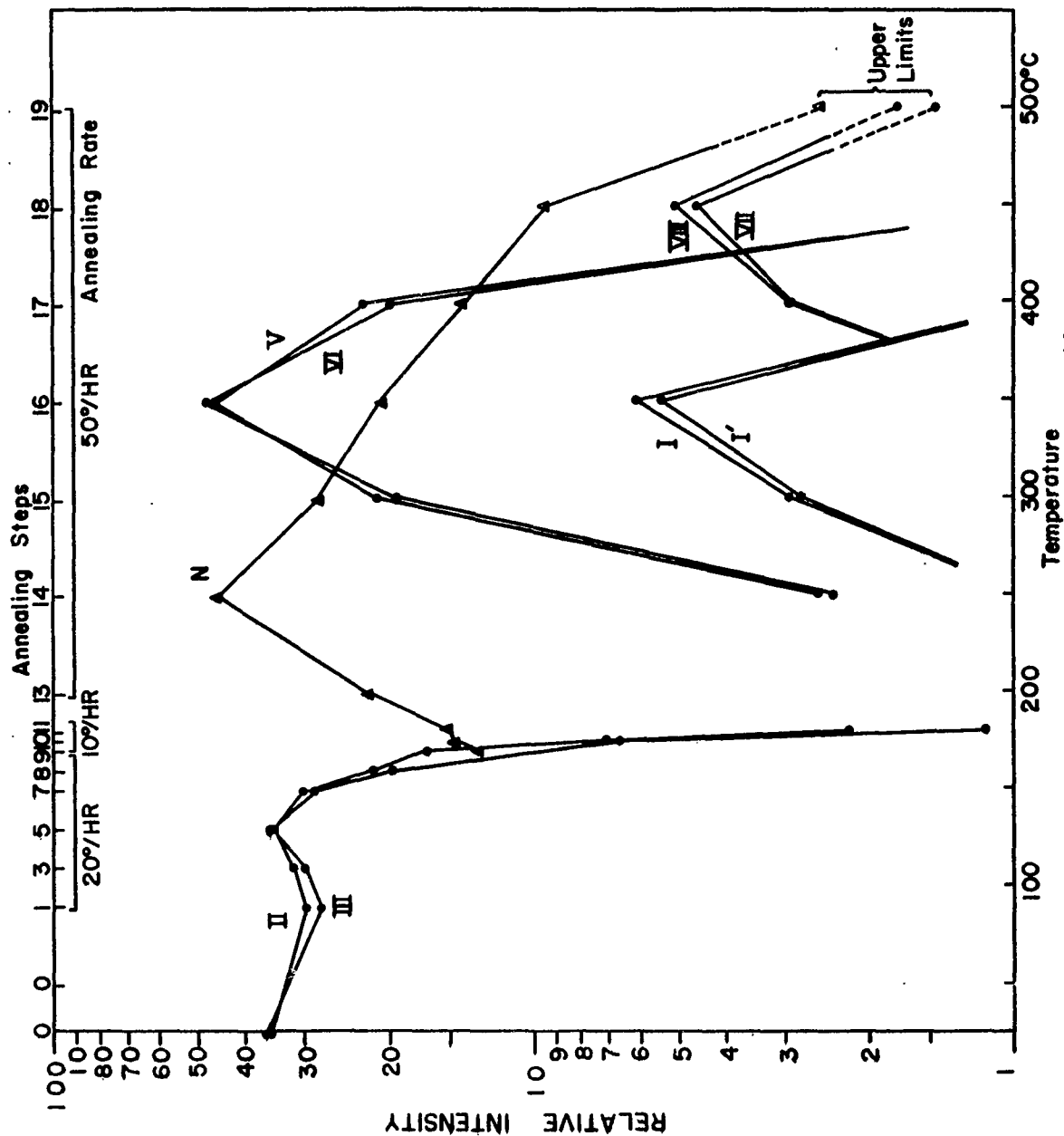


Fig. 6

Isochronal Anneal of Neutron  
Irradiated Silicon Relative EPR  
Amplitudes vs. Temperature  
US-SC #4,  $\phi = 1.4 \times 10^{18}$  nvt (ORNL)

To Estimate Absolute  
Concentration, Multiply  
Scale by  $1.24 \times 10^{13} (\Delta H)^2$

	$(\Delta H)^2$
II	1.44
III	1.44
N	1.44
V	1.44
VI	1.44
I	5.76
I'	5.76
VII	2.56
VIII	2.56

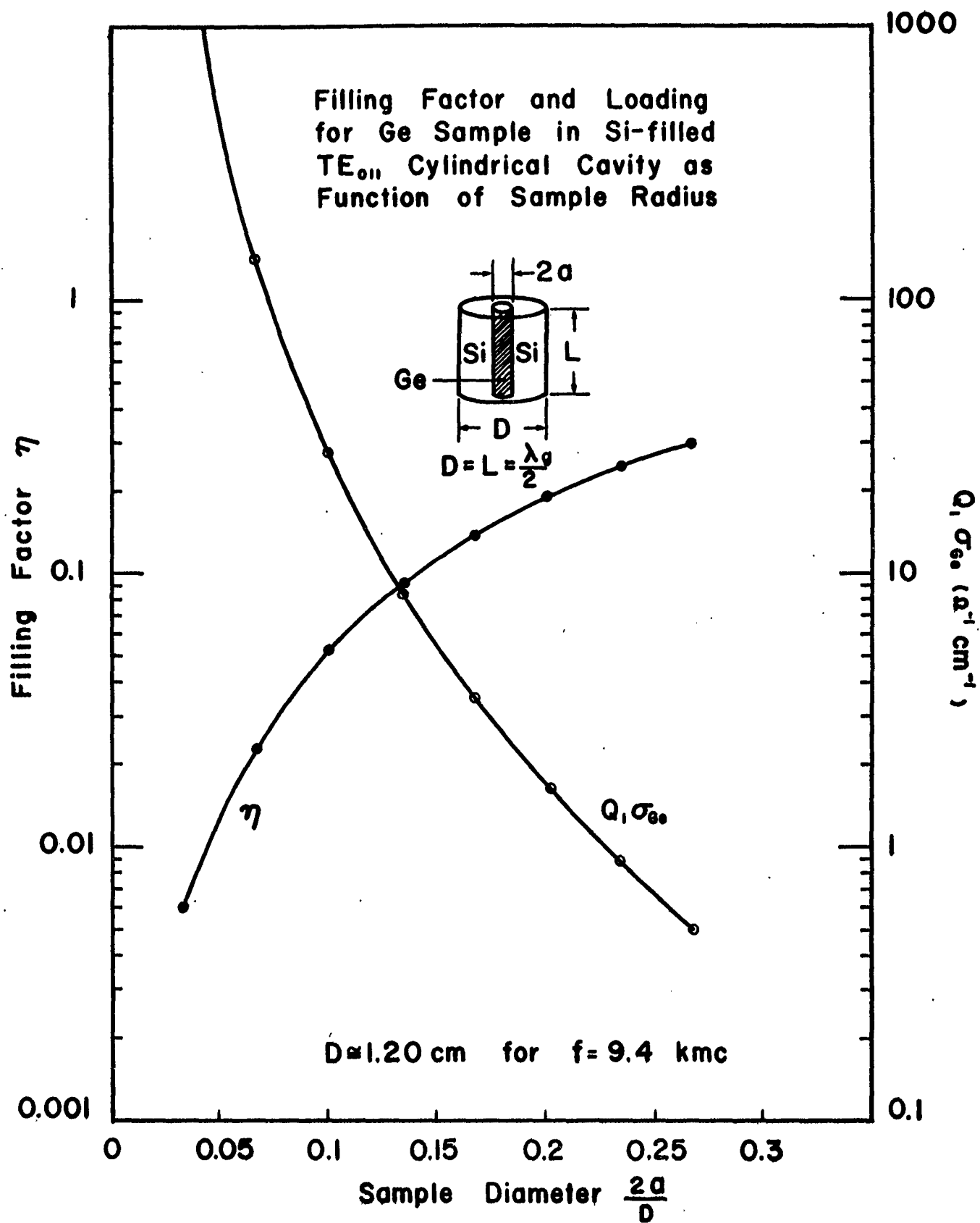


Fig. 7

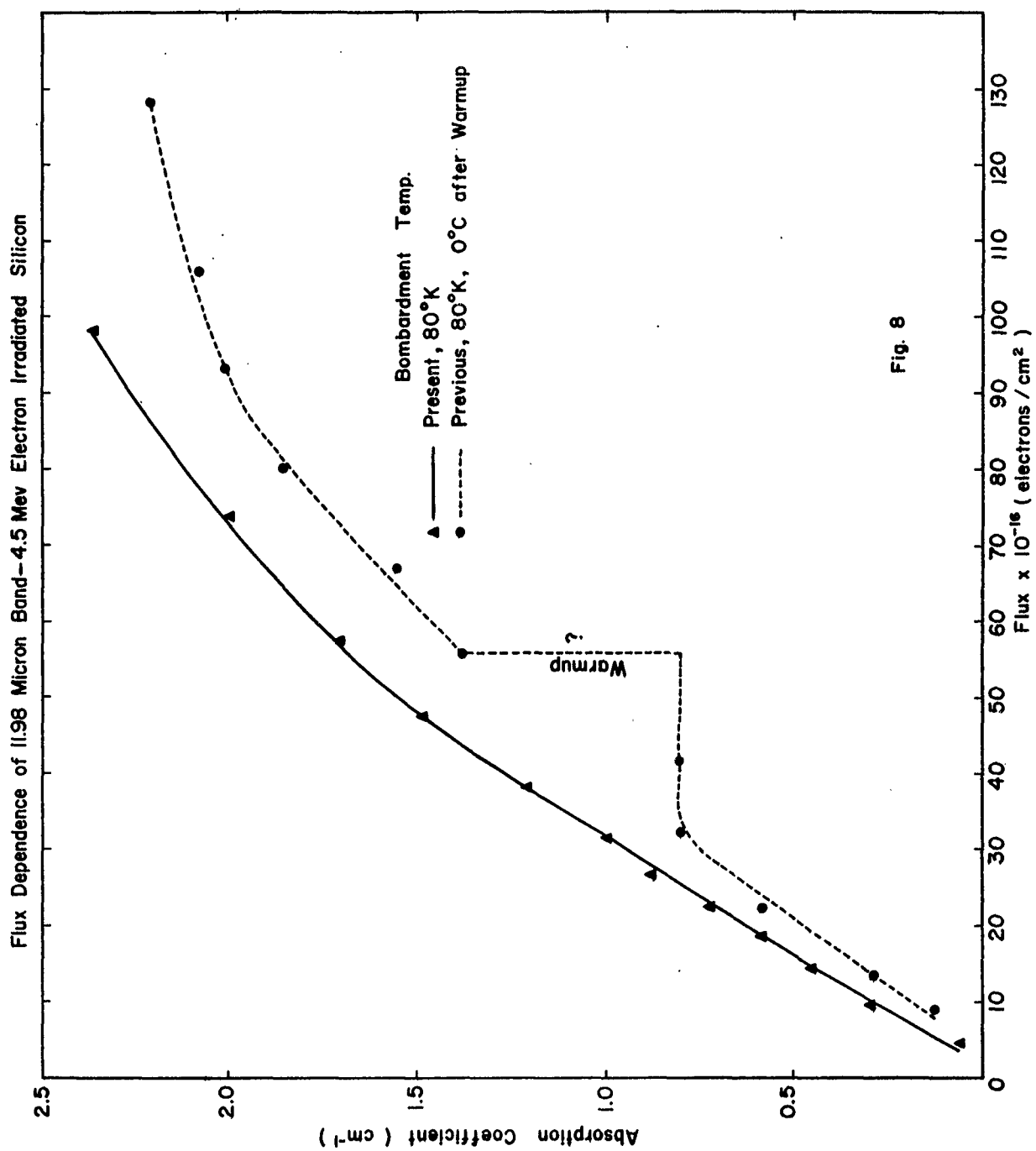


Fig. 8

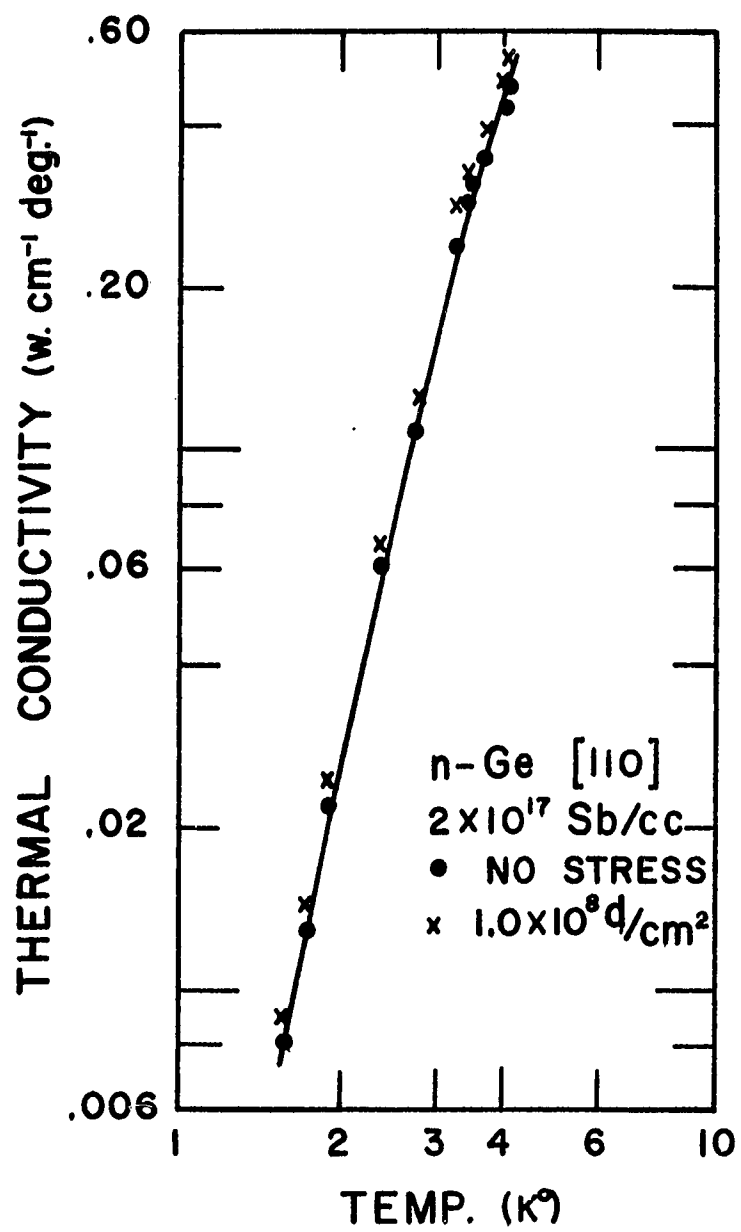


Fig. 9

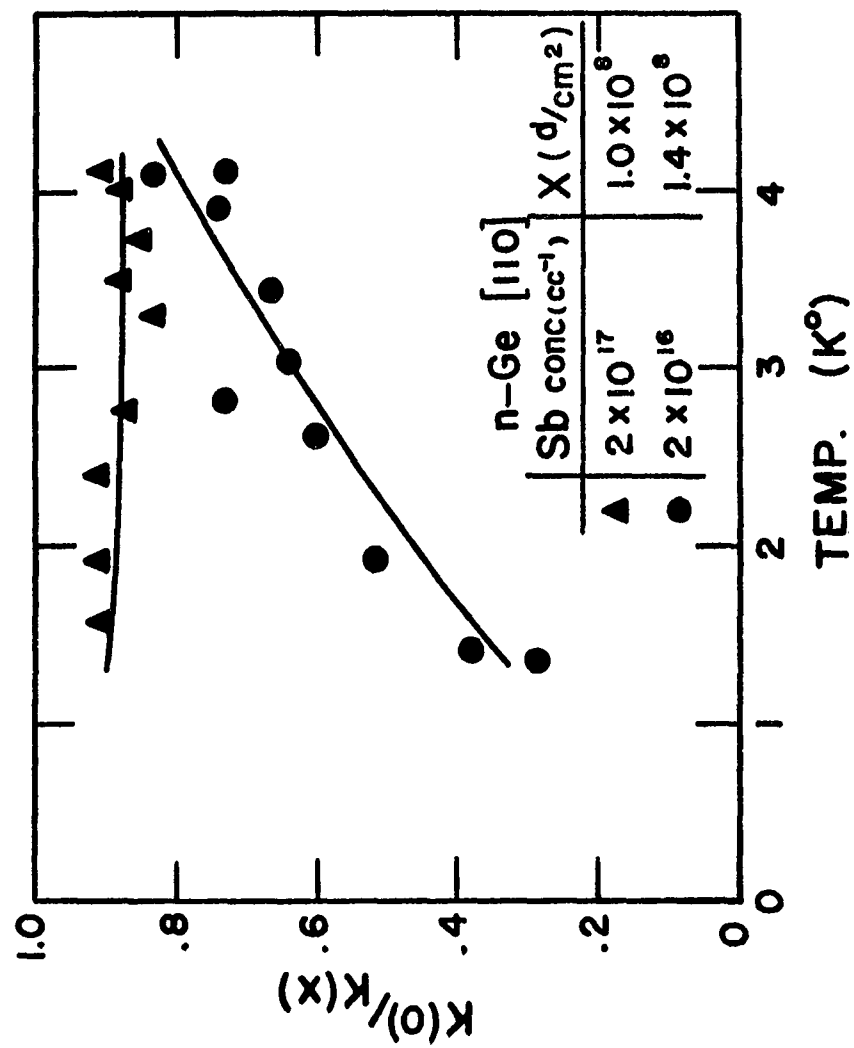


Fig. 10

# Ge THERMOMETER

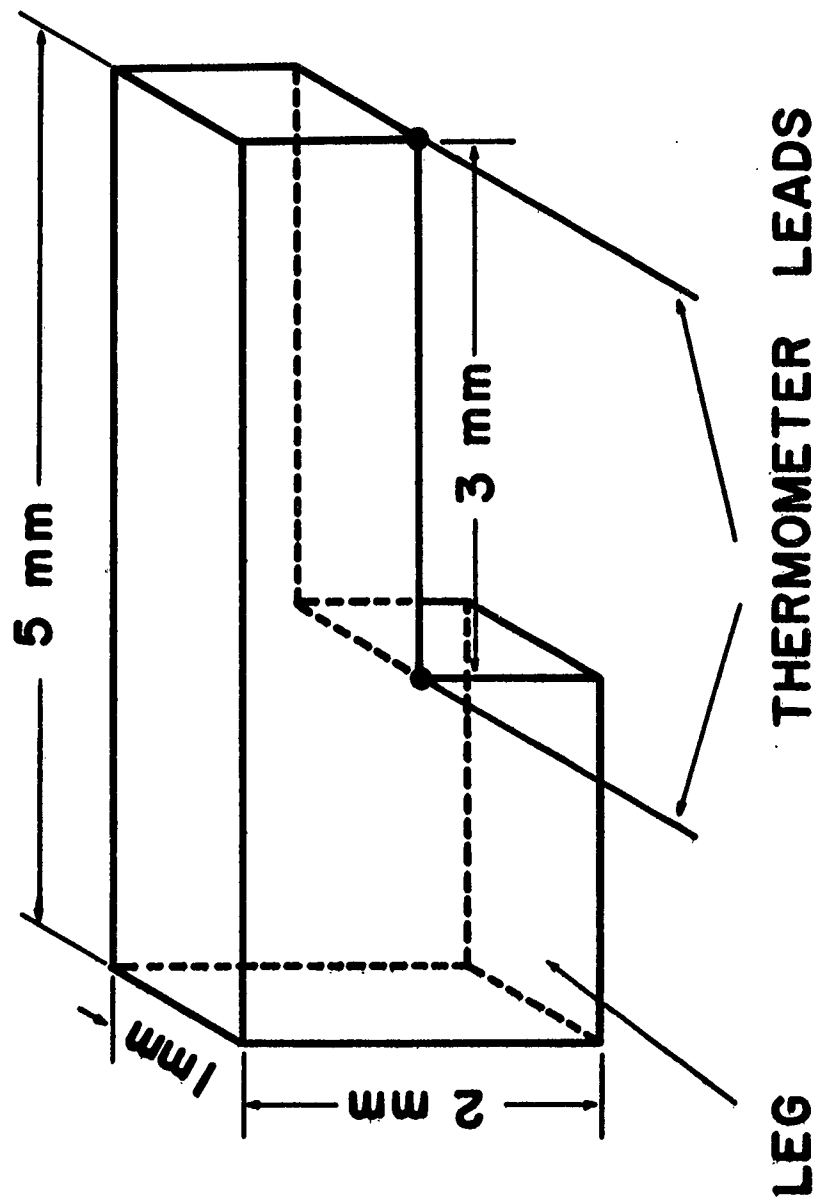


Fig. 11

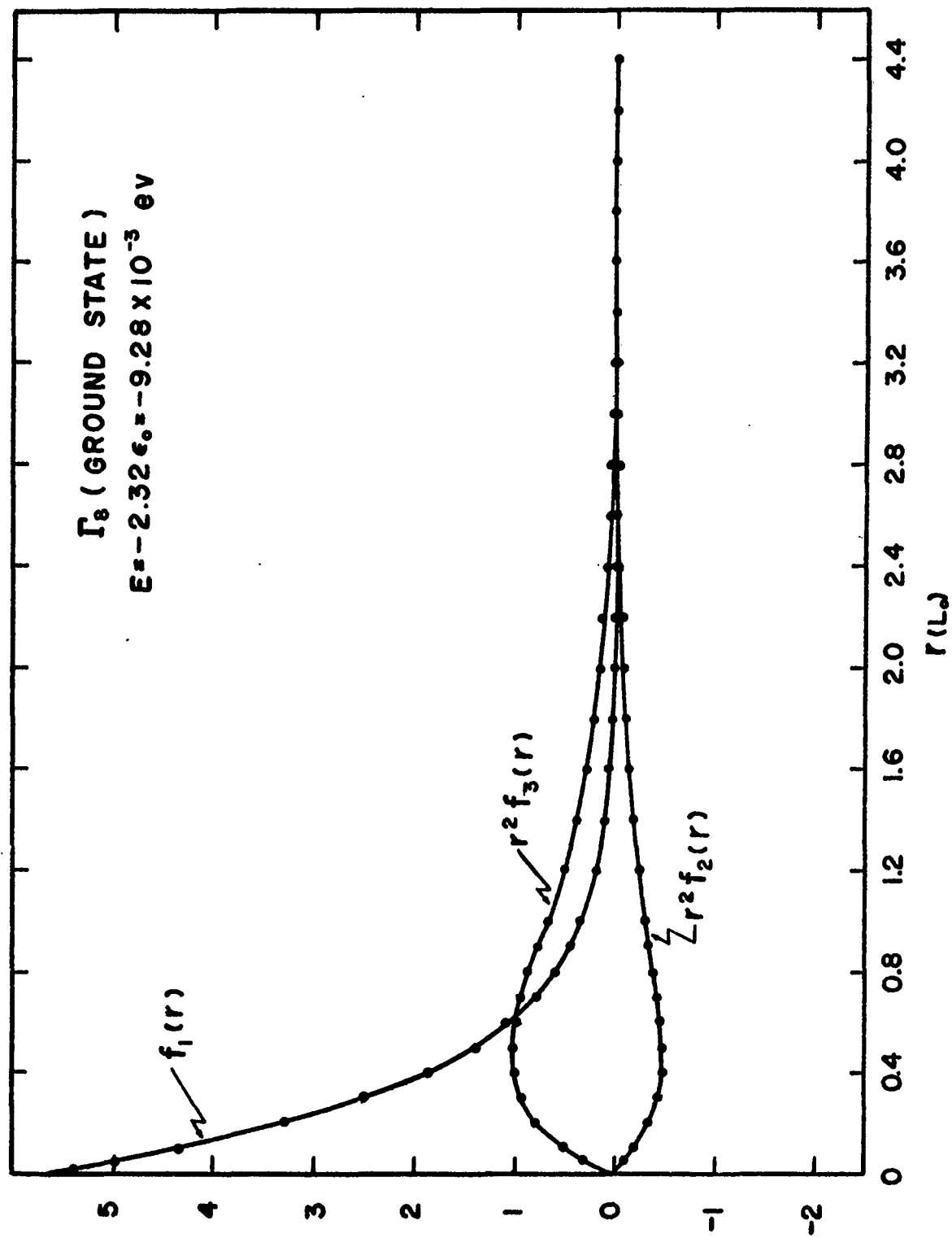


Fig. 12

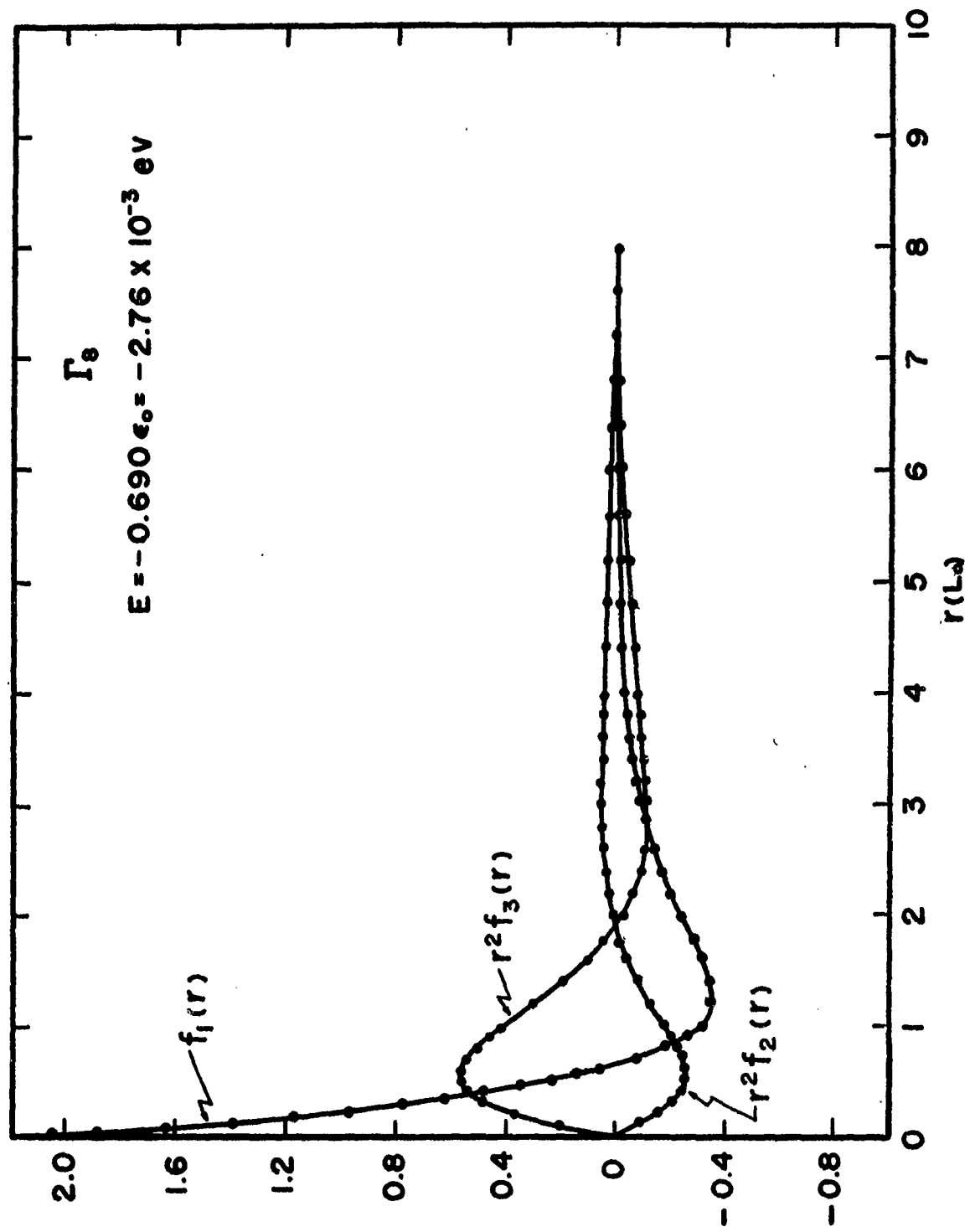


Fig. 13



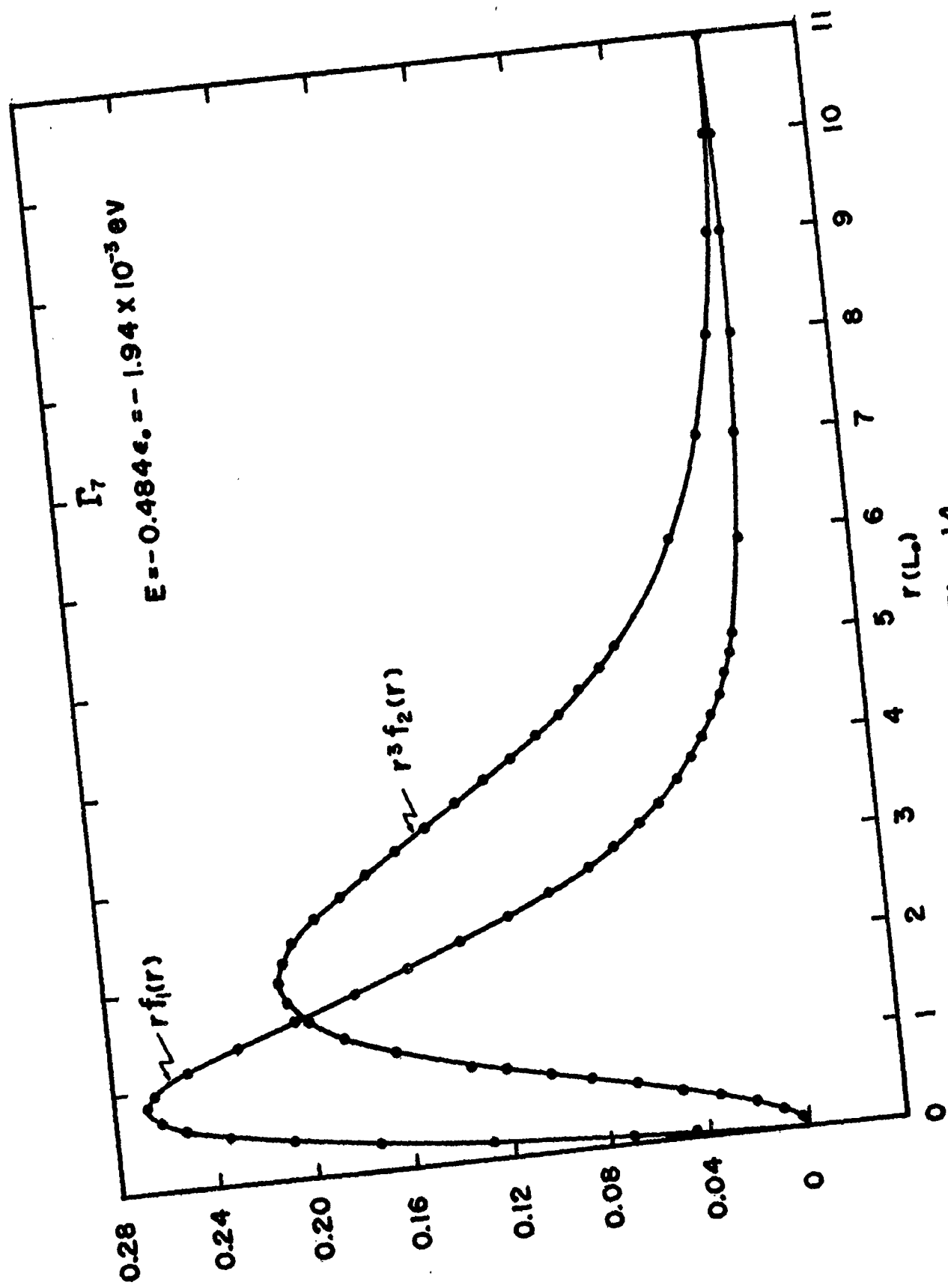


Fig. 14

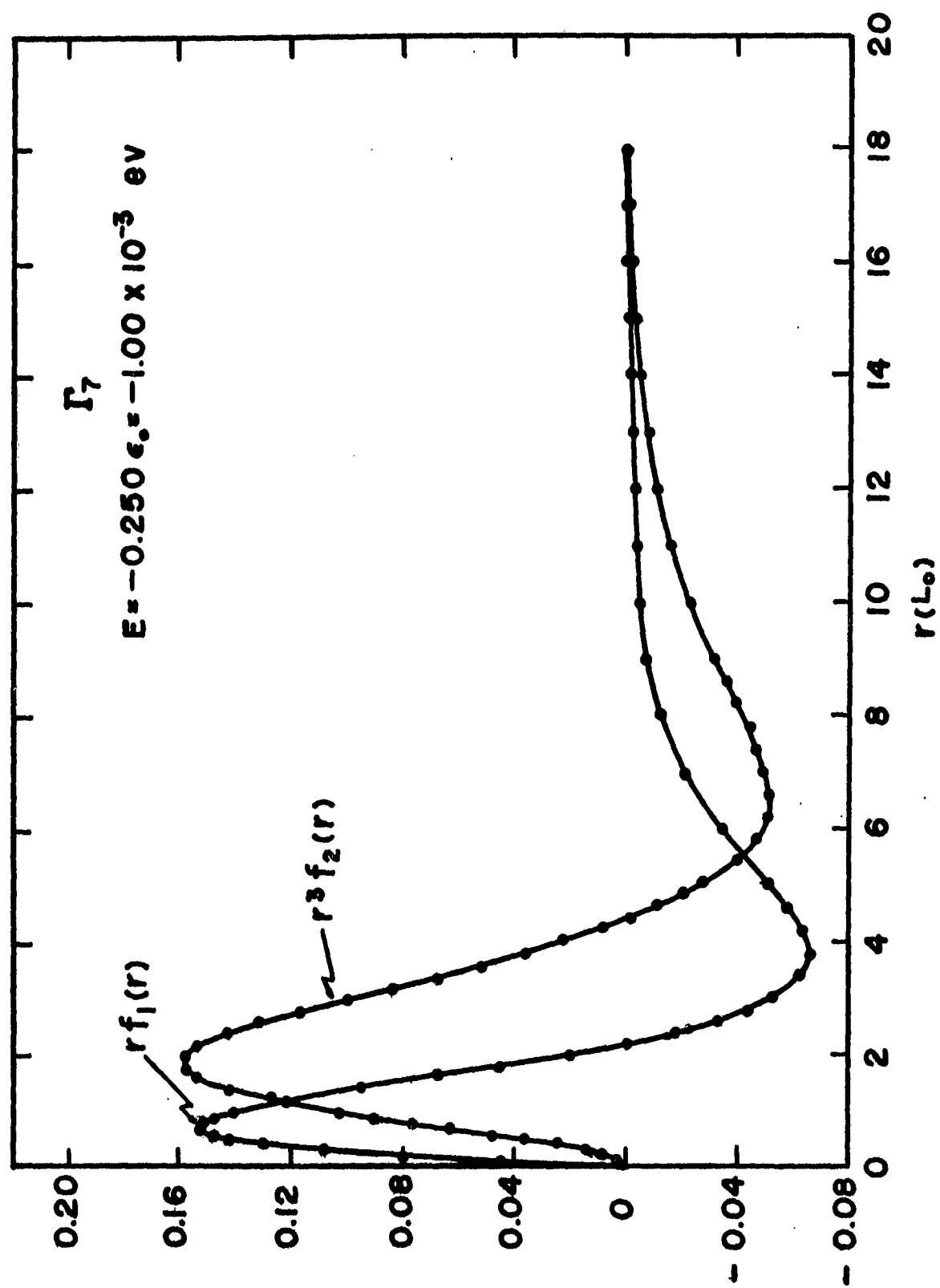


Fig. 15

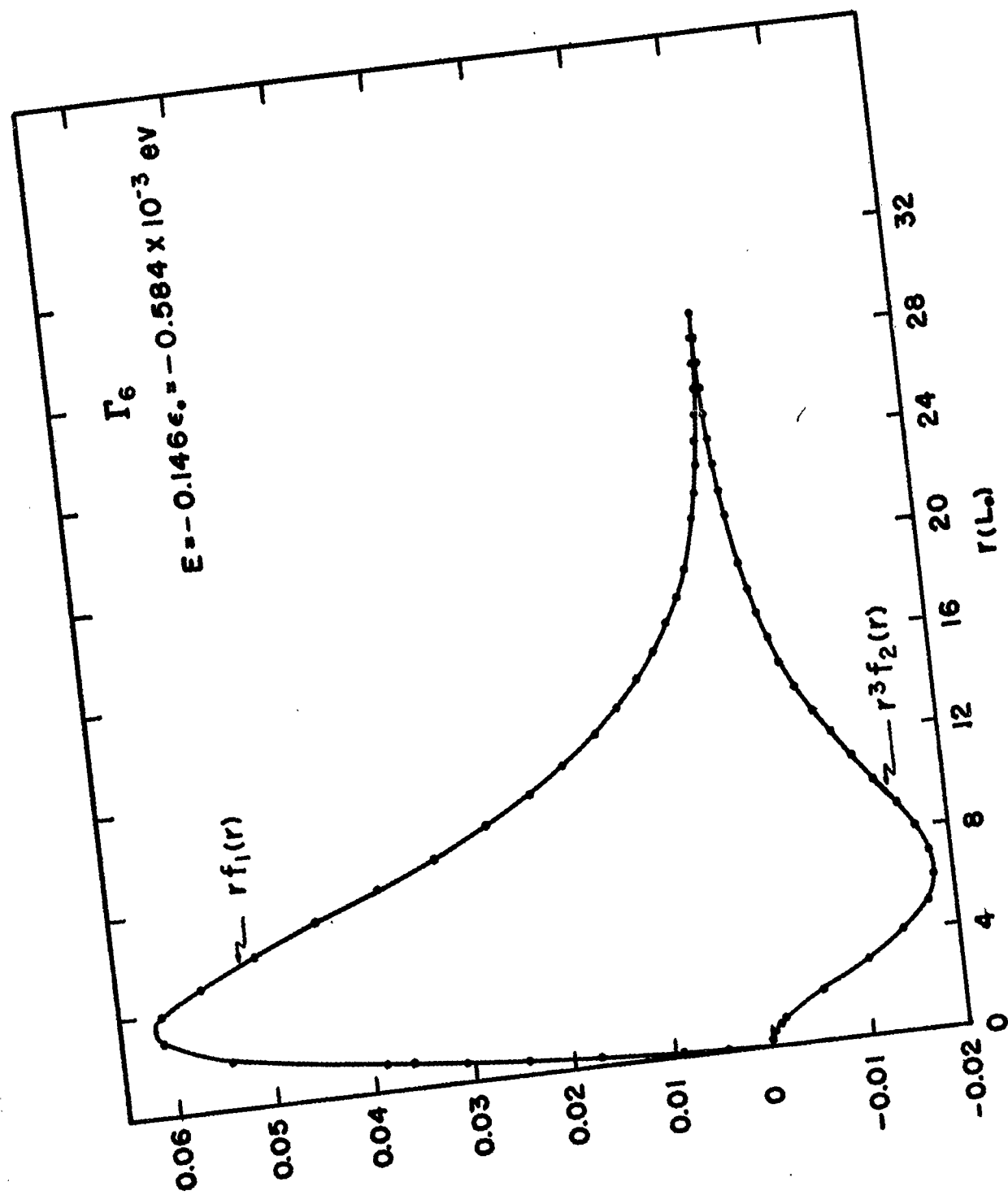


Fig. 16

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